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(54) **METHODS AND SYSTEMS FOR PROCESSING SUGAR MIXTURES AND RESULTANT COMPOSITIONS**

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(57) **ABSTRACT**

A method including: (a) selectively reacting a first sugar in a mixture which includes at least one second sugar to form a product mixture comprising a product of said first sugar; (b) separating said product of said first sugar from said product mixture; and (c) separating at least one of said at least one second sugar from said product mixture.

22 Claims, 16 Drawing Sheets

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Fig. 1

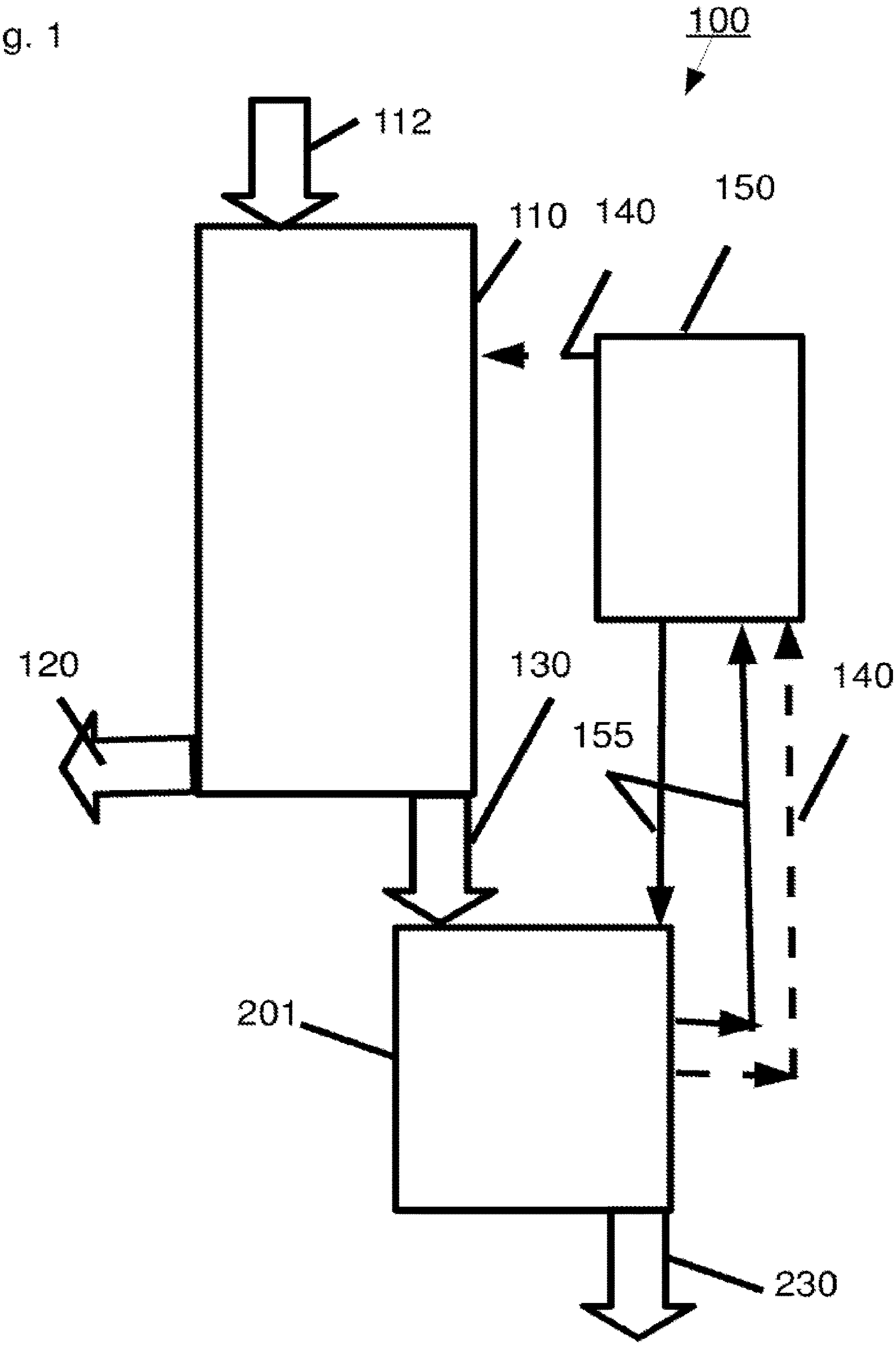


Fig. 2a

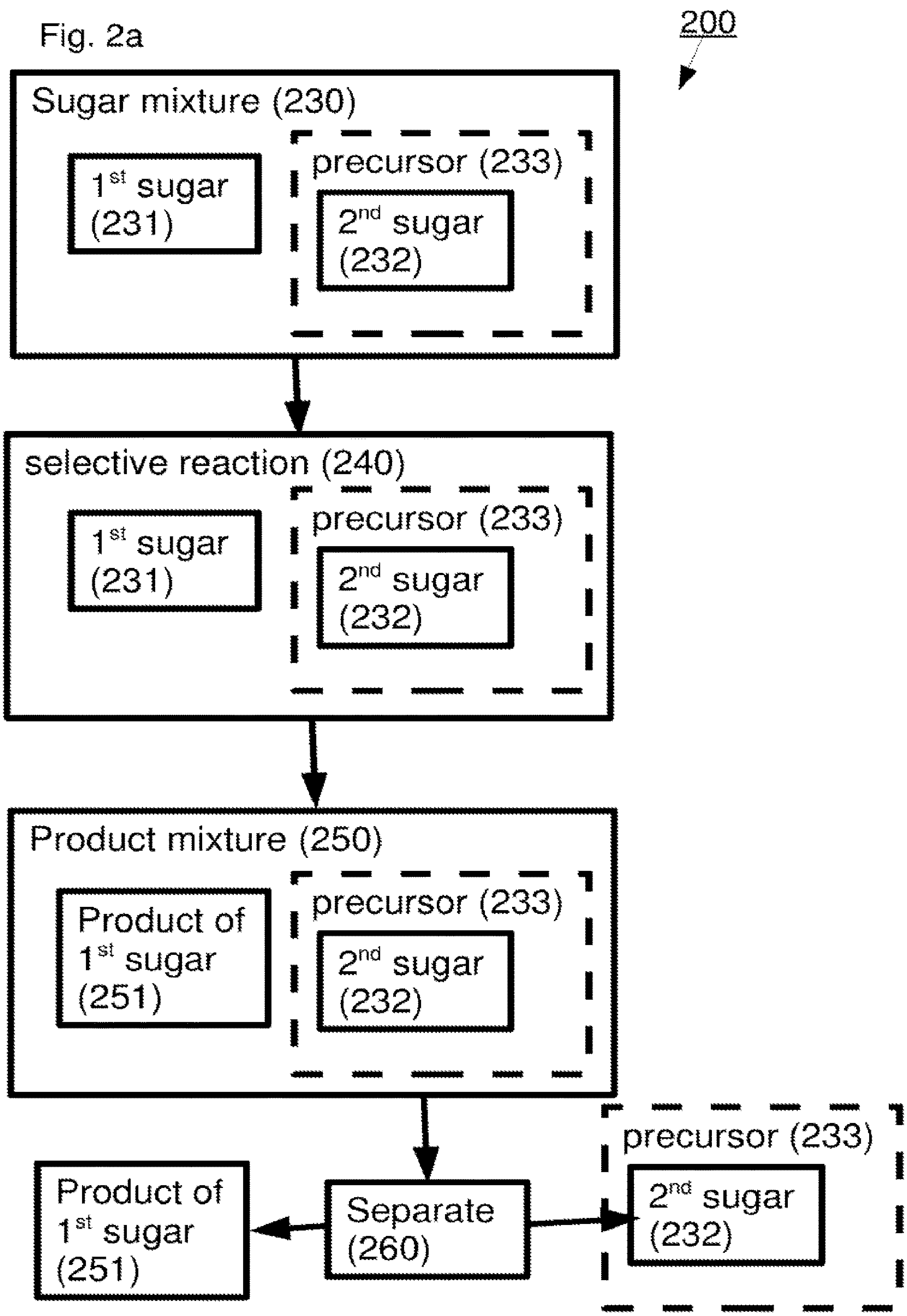

200
Sugar mixture (230)
1st sugar (231)
precursor (233)
2nd sugar (232)
selective reaction (240)
1st sugar (231)
precursor (233)
2nd sugar (232)
Product mixture (250)
Product of 1st sugar (251)
precursor (233)
2nd sugar (232)
Product of 1st sugar (251)
Separate (260)
precursor (233)
2nd sugar (232)

Fig. 2b

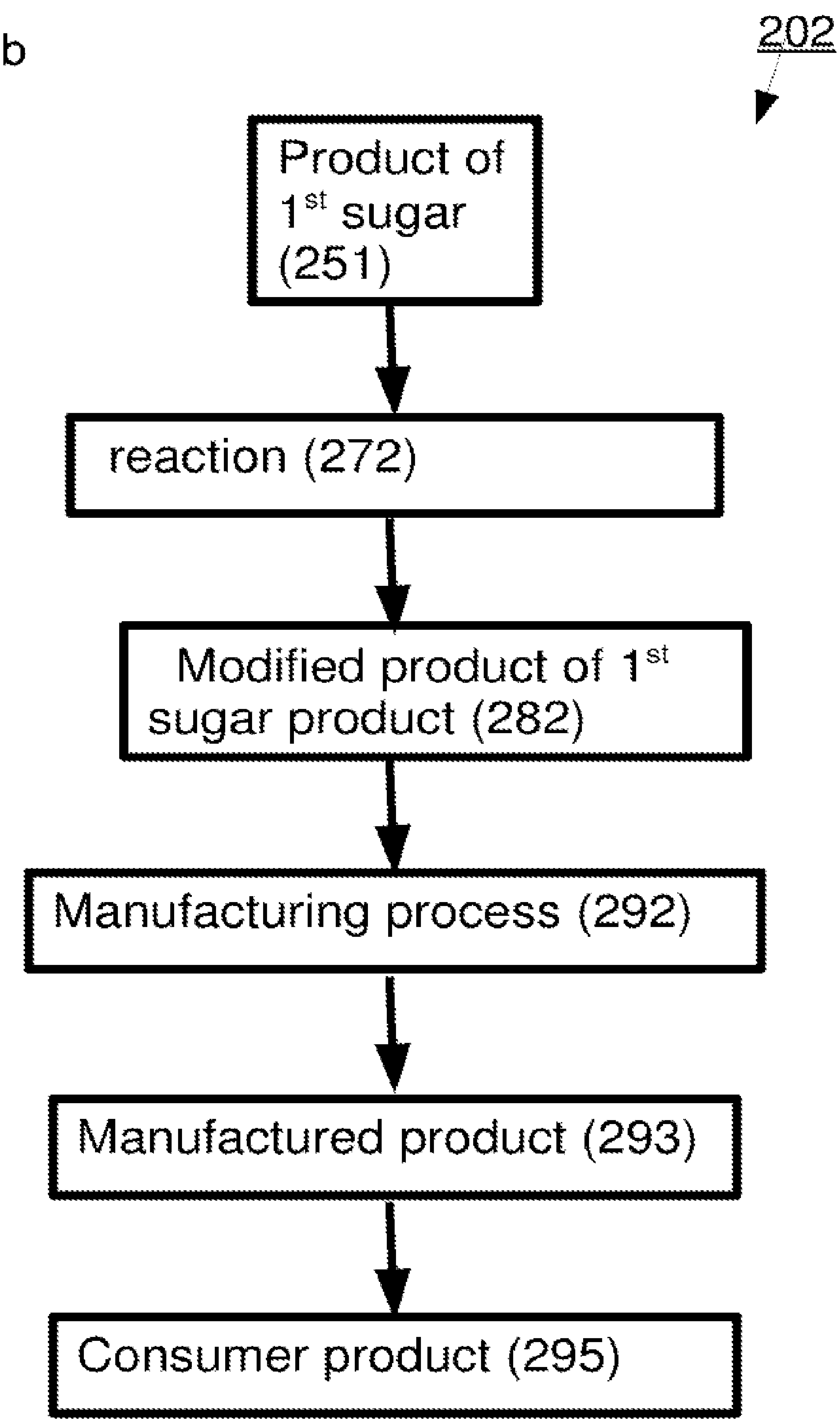

202
Product of 1st sugar (251)
reaction (272)
Modified product of 1st sugar product (282)
Manufacturing process (292)
Manufactured product (293)
Consumer product (295)

Fig. 2c

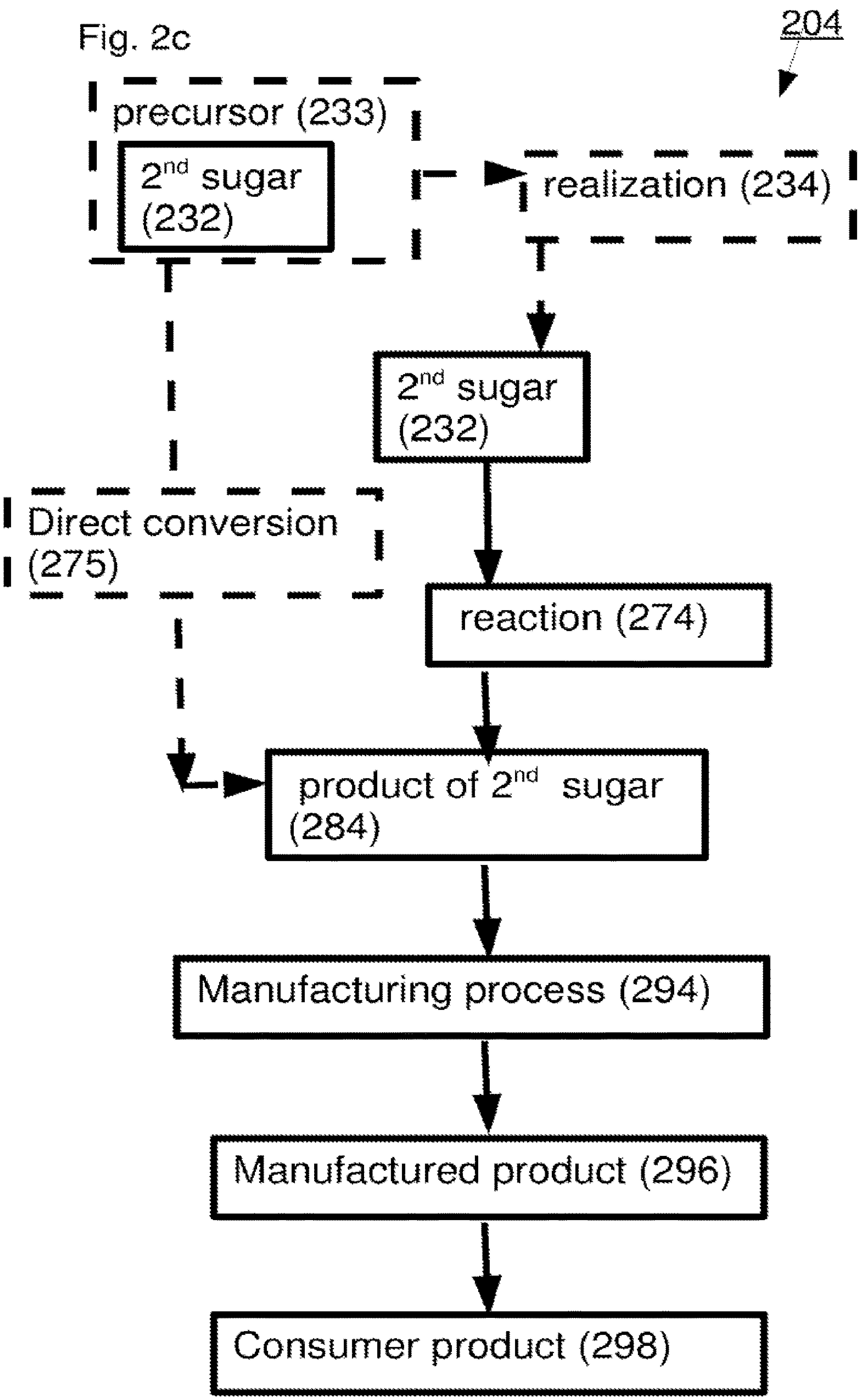

204
precursor (233)
2nd sugar (232)
realization (234)
2nd sugar (232)
Direct conversion (275)
reaction (274)
product of 2nd sugar (284)
Manufacturing process (294)
Manufactured product (296)
Consumer product (298)

Fig. 3

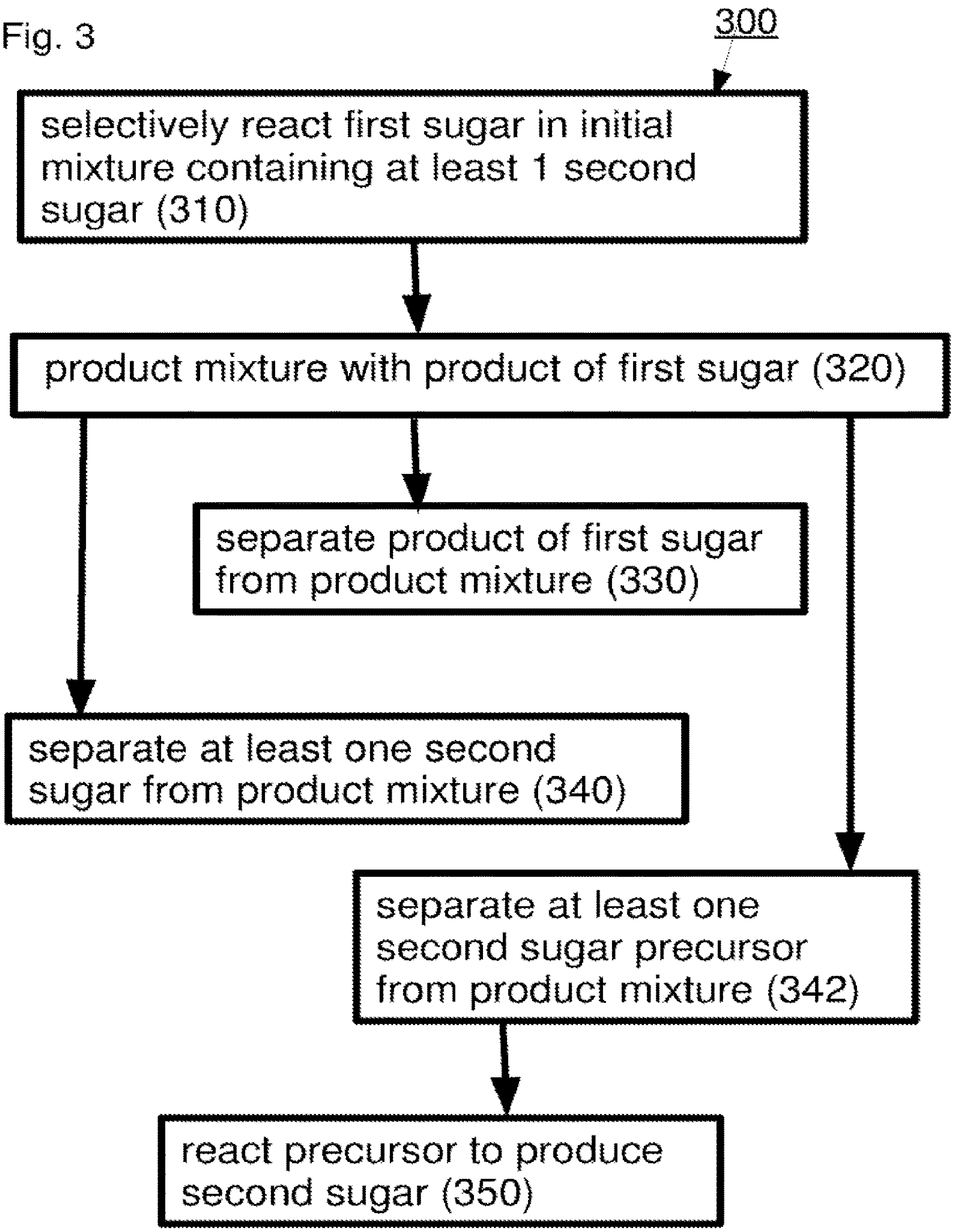

300
selectively react first sugar in initial mixture containing at least 1 second sugar (310)
product mixture with product of first sugar (320)
separate product of first sugar from product mixture (330)
separate at least one second sugar from product mixture (340)
separate at least one second sugar precursor from product mixture (342)
react precursor to produce second sugar (350)

Fig. 4

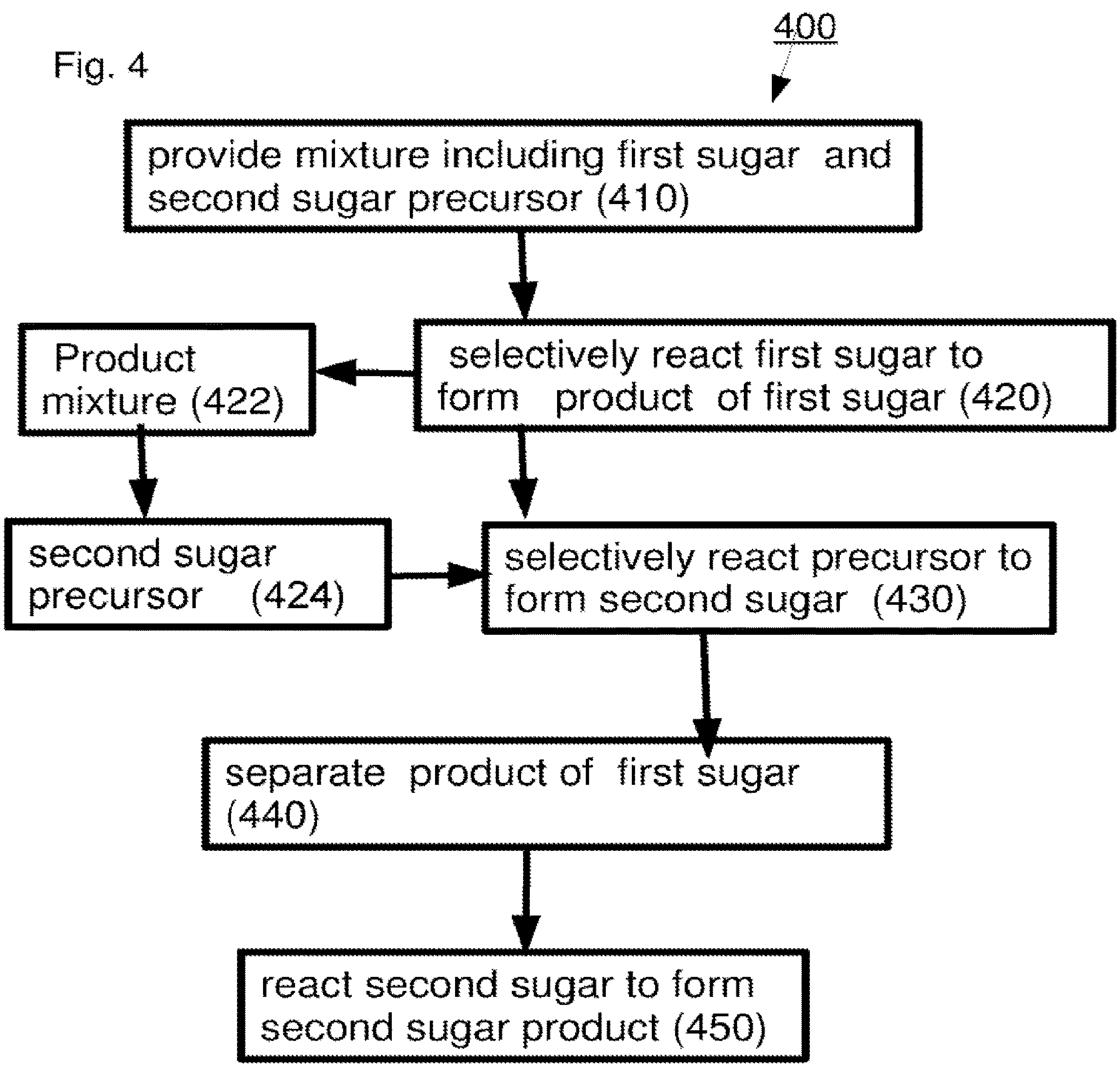

400
provide mixture including first sugar and second sugar precursor (410)
selectively react first sugar to form product of first sugar (420)
Product mixture (422)
second sugar precursor (424)
selectively react precursor to form second sugar (430)
separate product of first sugar (440)
react second sugar to form second sugar product (450)

Fig. 5

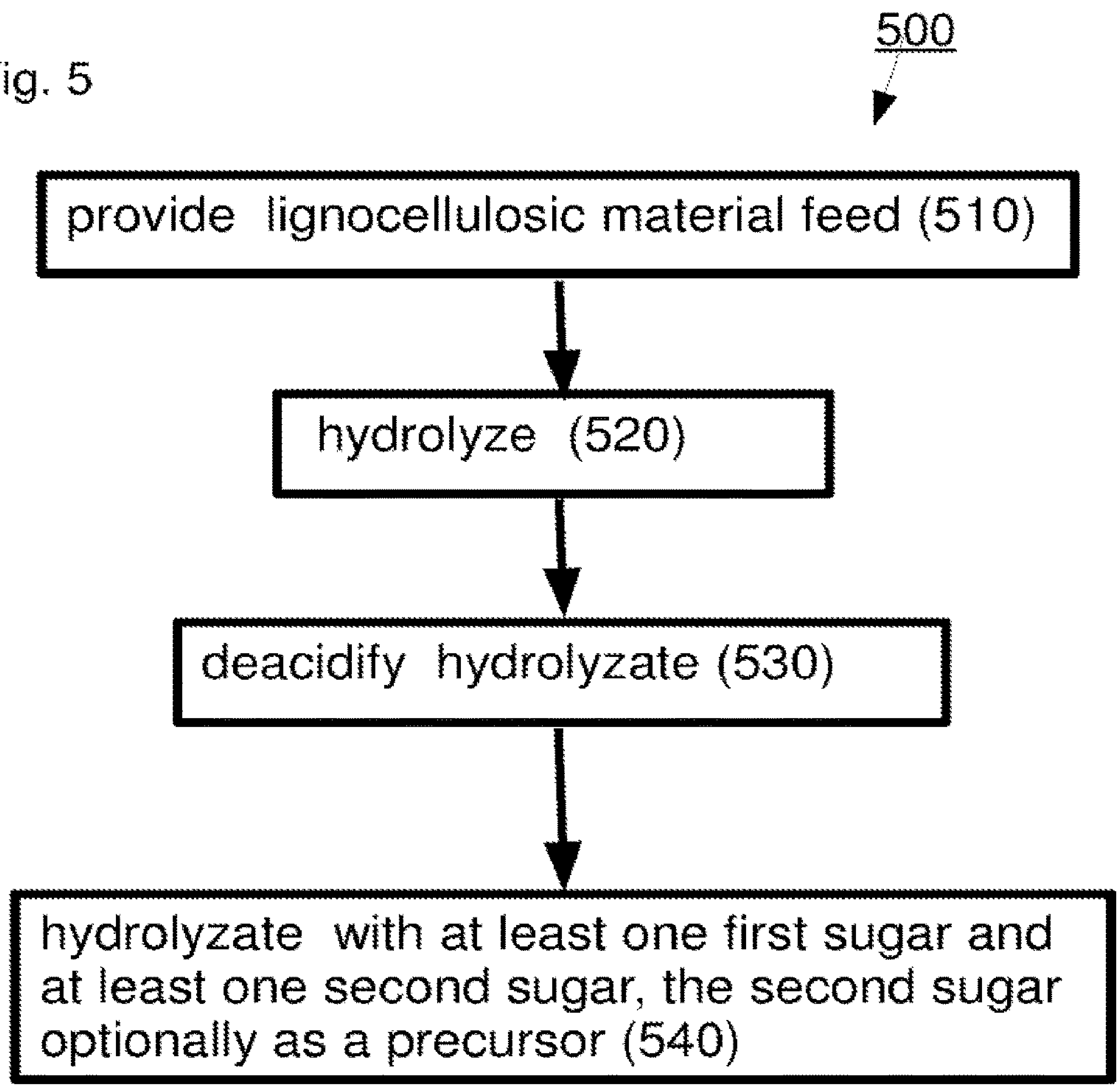

500
provide lignocellulosic material feed (510)
hydrolyze (520)
deacidify hydrolyzate (530)
hydrolyzate with at least one first sugar and at least one second sugar, the second sugar optionally as a precursor (540)

Fig. 6a

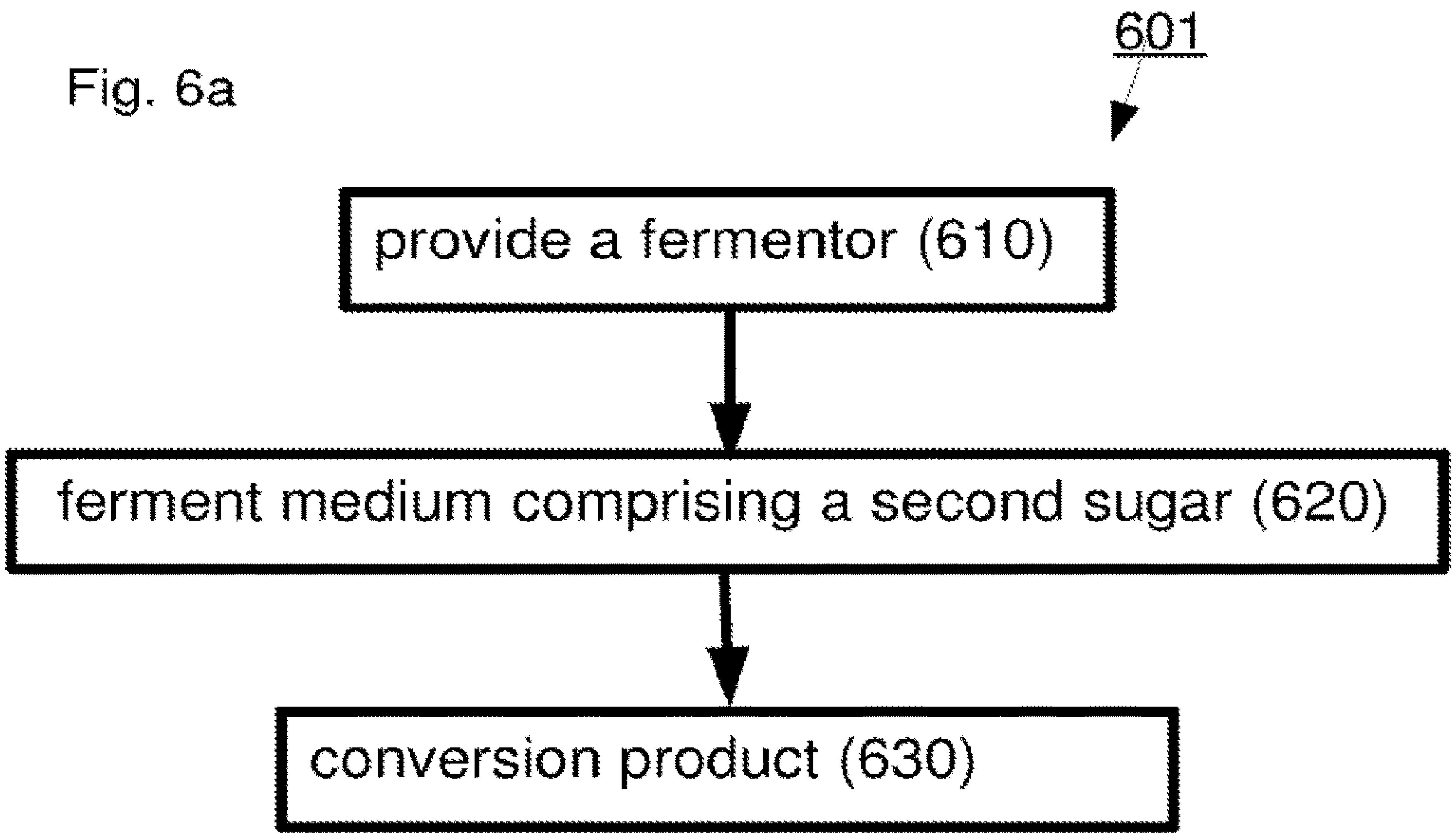

601
provide a fermentor (610)
ferment medium comprising a second sugar (620)
conversion product (630)

Fig. 6b

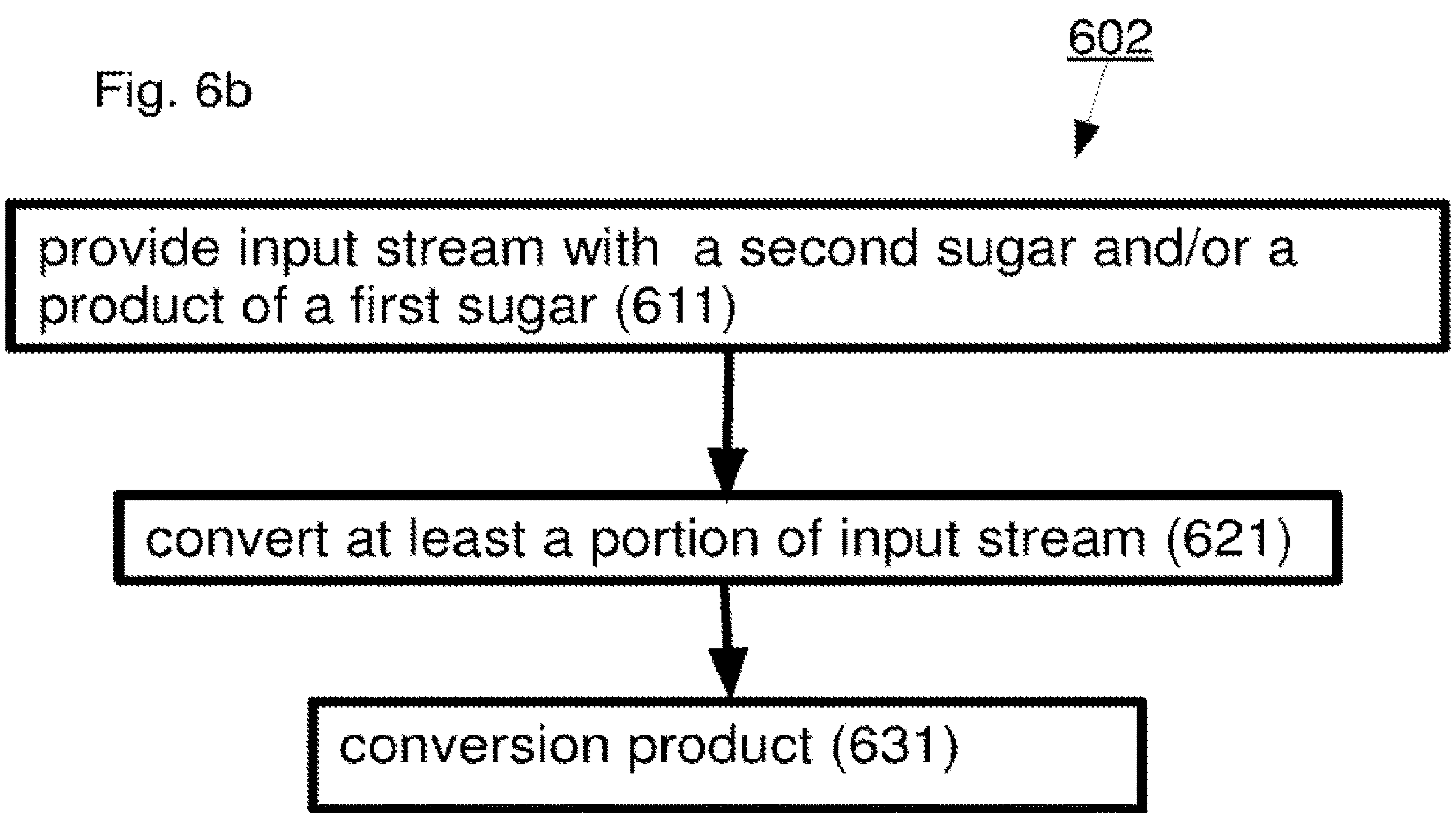

602
provide input stream with a second sugar and/or a product of a first sugar (611)
convert at least a portion of input stream (621)
conversion product (631)

Fig. 7a

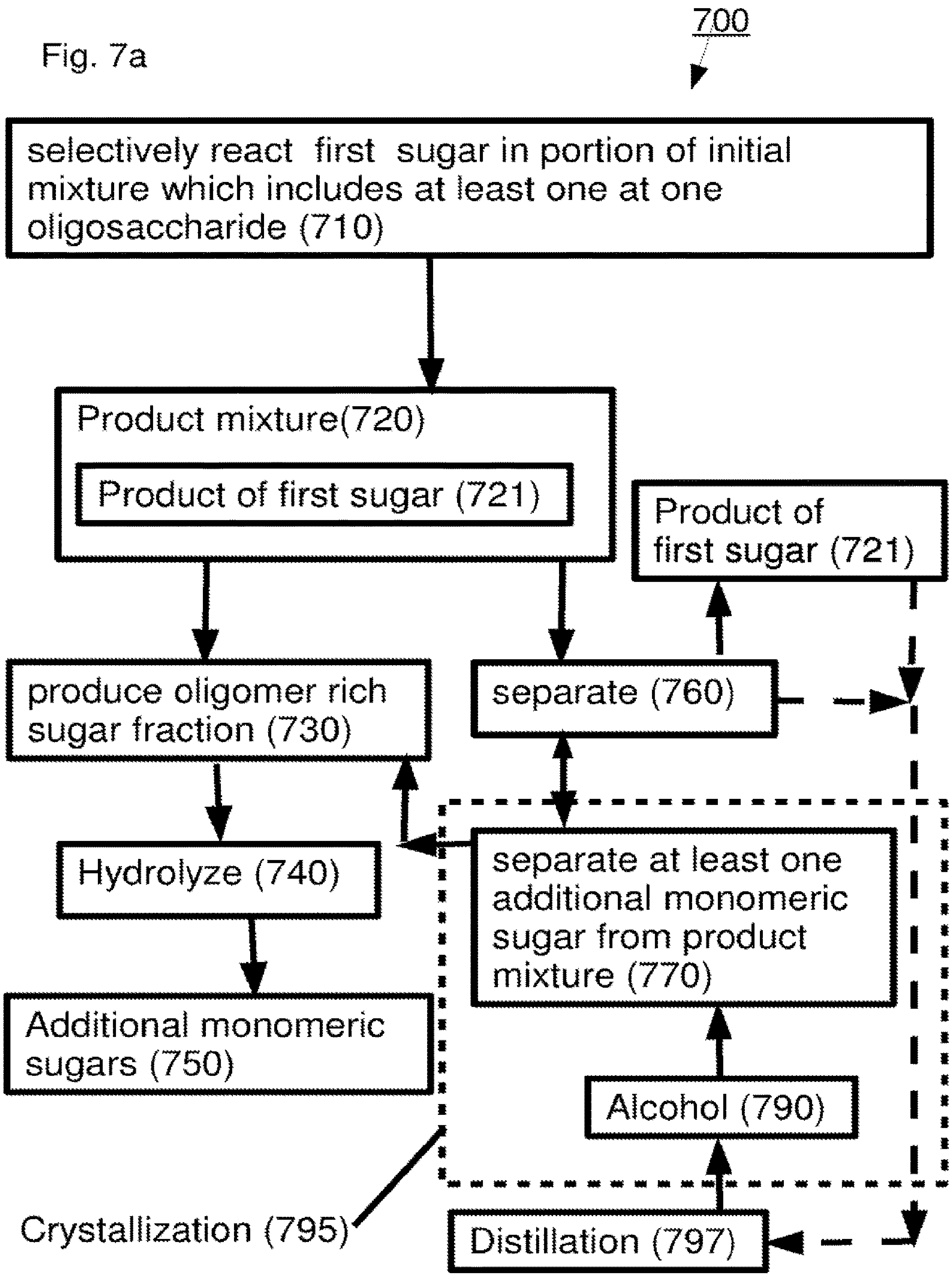

700
selectively react first sugar in portion of initial mixture which includes at least one at one oligosaccharide (710)
Product mixture(720)
Product of first sugar (721)
Product of first sugar (721)
produce oligomer rich sugar fraction (730)
separate (760)
Hydrolyze (740)
separate at least one additional monomeric sugar from product mixture (770)
Additional monomeric sugars (750)
Alcohol (790)
Crystallization (795)
Distillation (797)

Fig. 7b

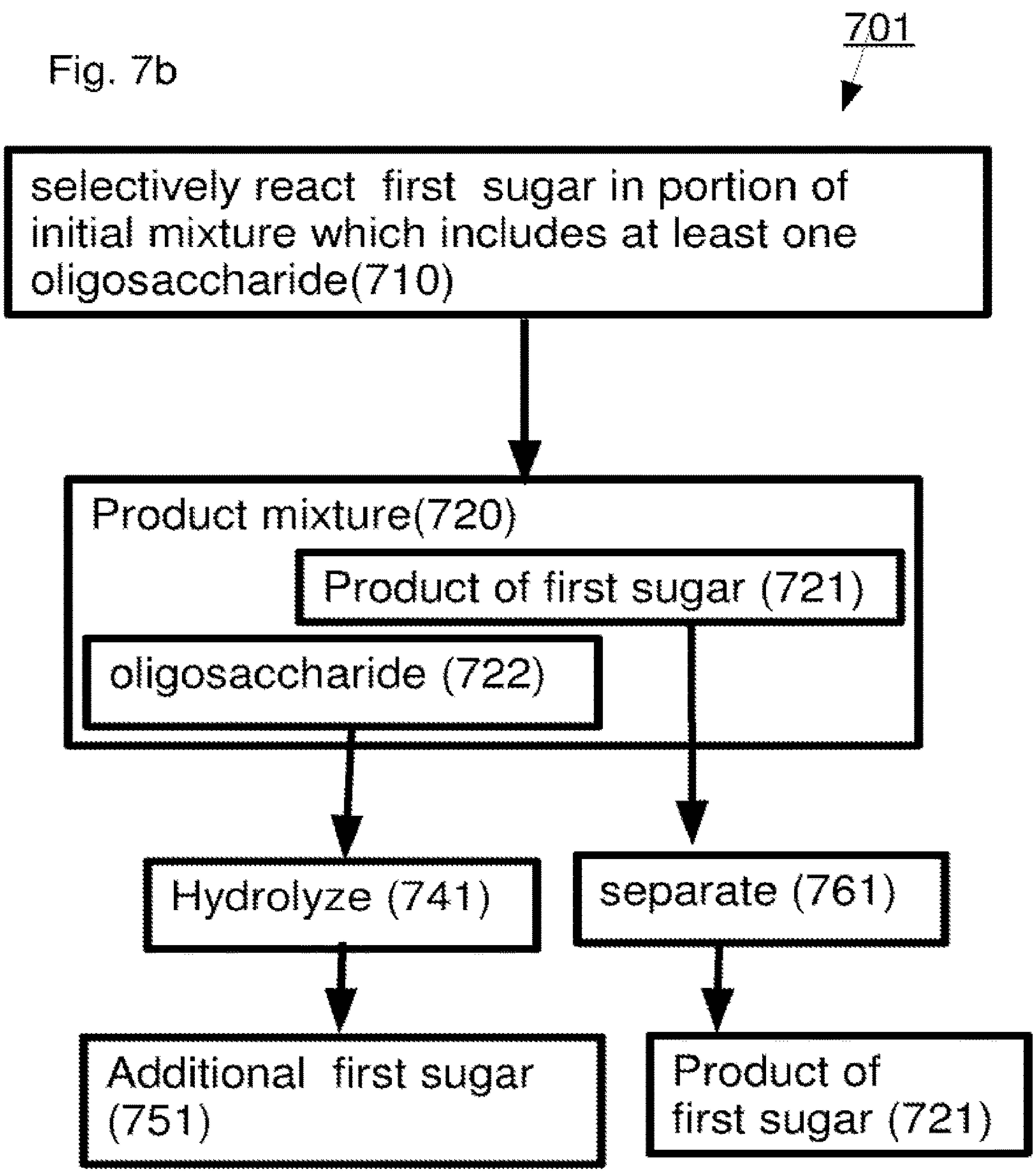

701
selectively react first sugar in portion of initial mixture which includes at least one oligosaccharide(710)
Product mixture(720)
Product of first sugar (721)
oligosaccharide (722)
Hydrolyze (741)
separate (761)
Additional first sugar (751)
Product of first sugar (721)

Fig. 8a

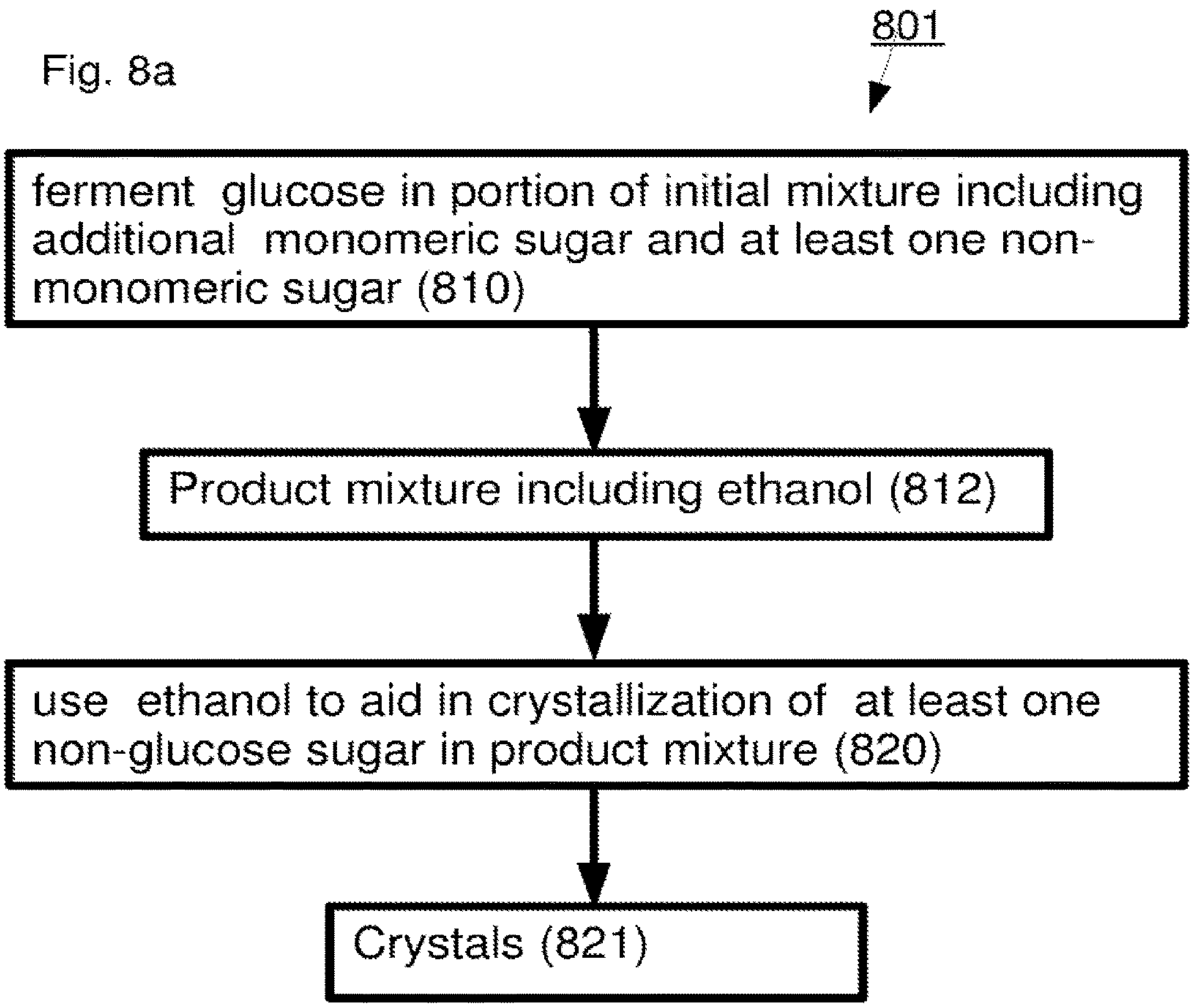

801
ferment glucose in portion of initial mixture including additional monomeric sugar and at least one non-monomeric sugar (810)
Product mixture including ethanol (812)
use ethanol to aid in crystallization of at least one non-glucose sugar in product mixture (820)
Crystals (821)

Fig. 8b

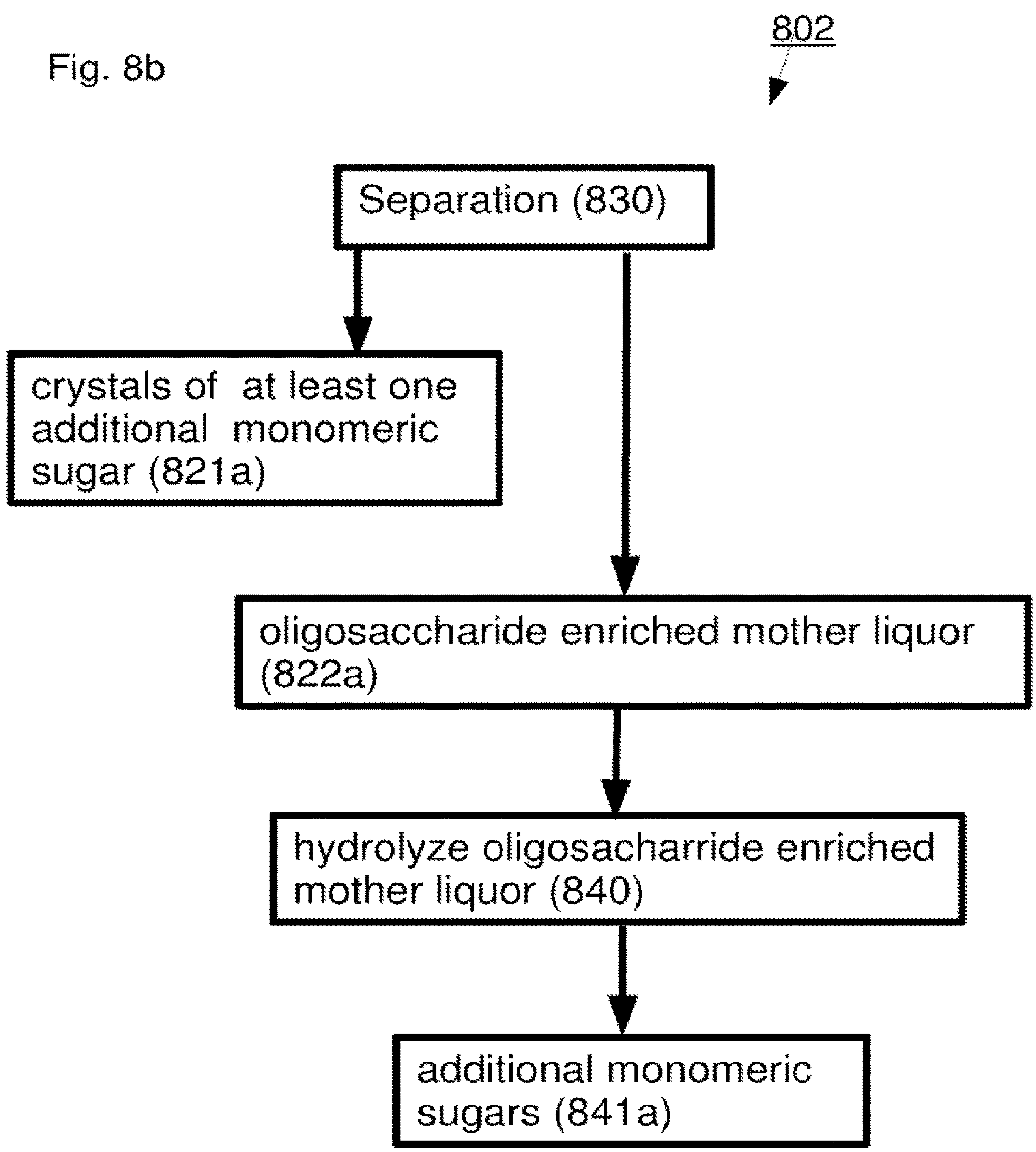

802
Separation (830)
crystals of at least one additional monomeric sugar (821a)
oligosaccharide enriched mother liquor (822a)
hydrolyze oligosacharride enriched mother liquor (840)
additional monomeric sugars (841a)

Fig. 8c

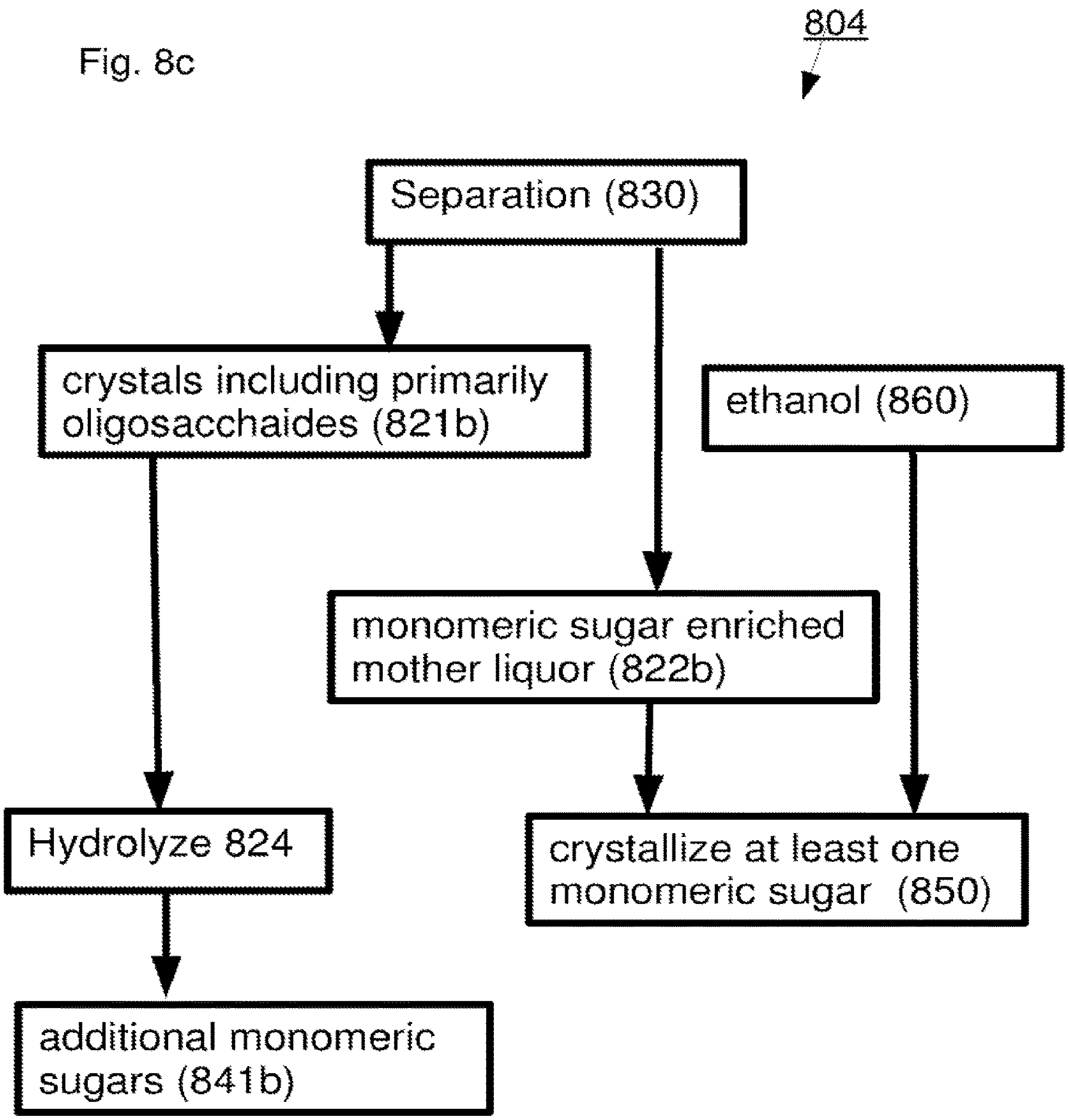

804
Separation (830)
crystals including primarily oligosacchaides (821b)
ethanol (860)
monomeric sugar enriched mother liquor (822b)
Hydrolyze 824
crystallize at least one monomeric sugar (850)
additional monomeric sugars (841b)

Fig. 9

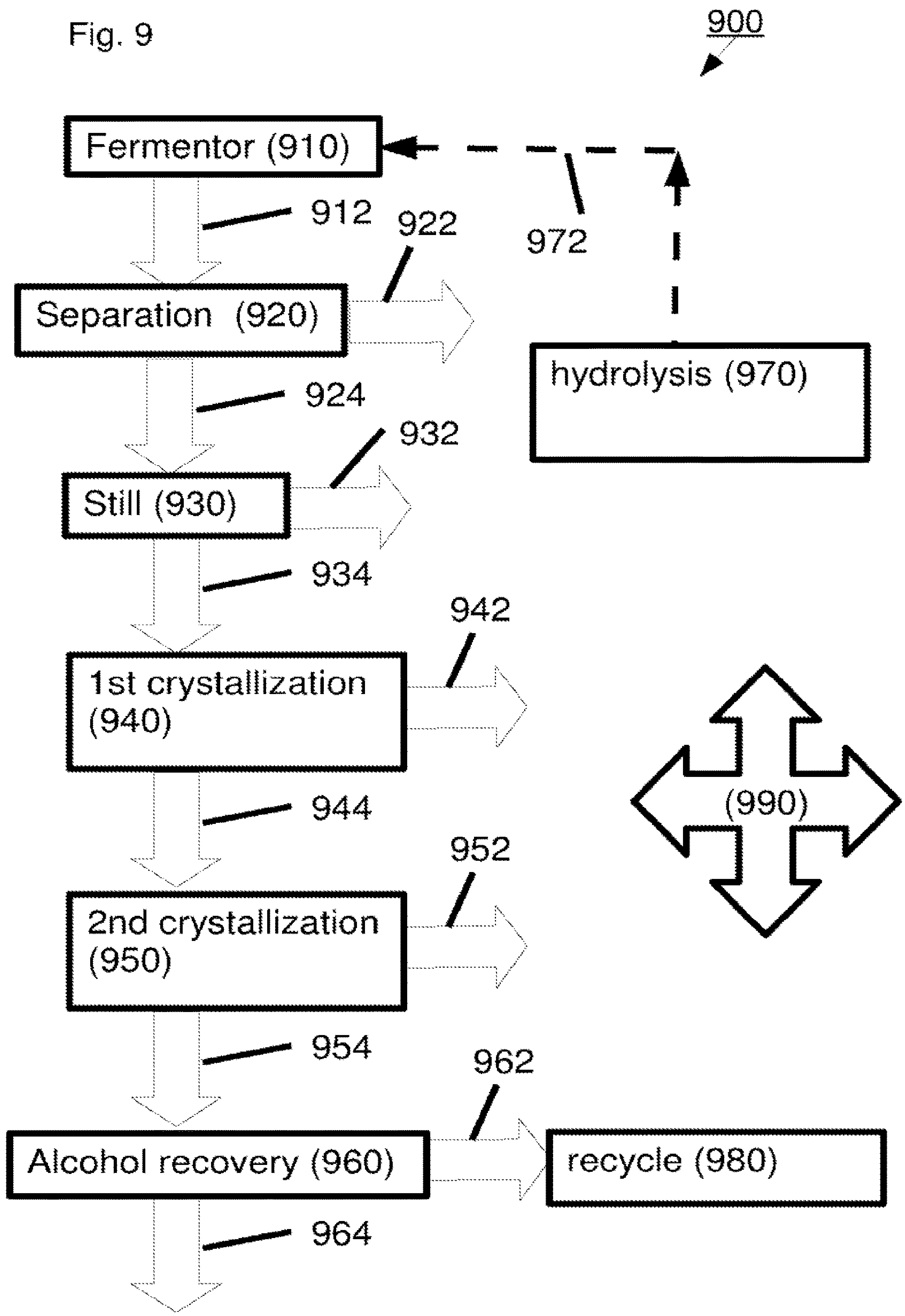

900
Fermentor (910)
912
922
972
Separation (920)
hydrolysis (970)
924
932
Still (930)
934
942
1st crystallization (940)
(990)
944
952
2nd crystallization (950)
954
962
Alcohol recovery (960)
recycle (980)
964

Fig. 10

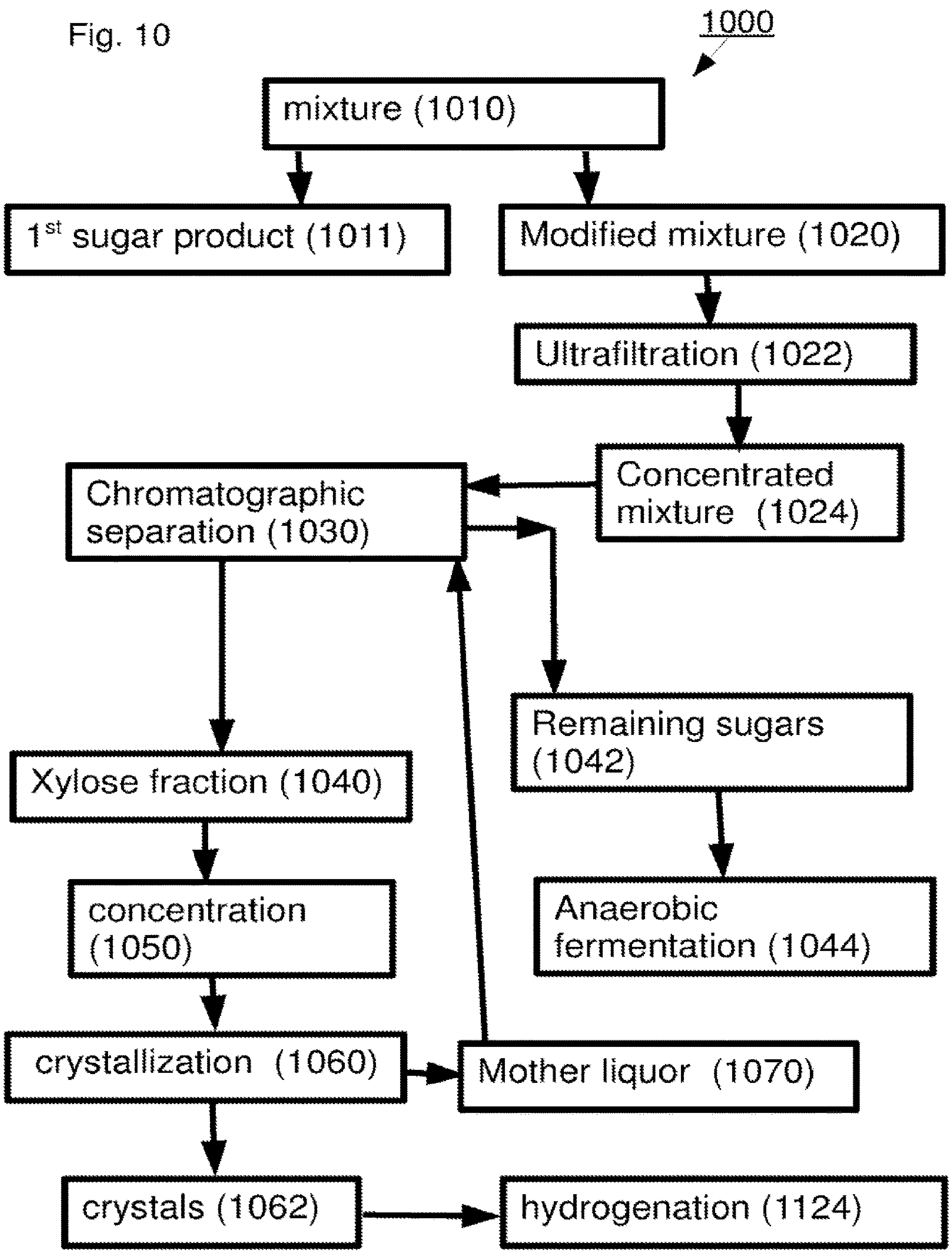
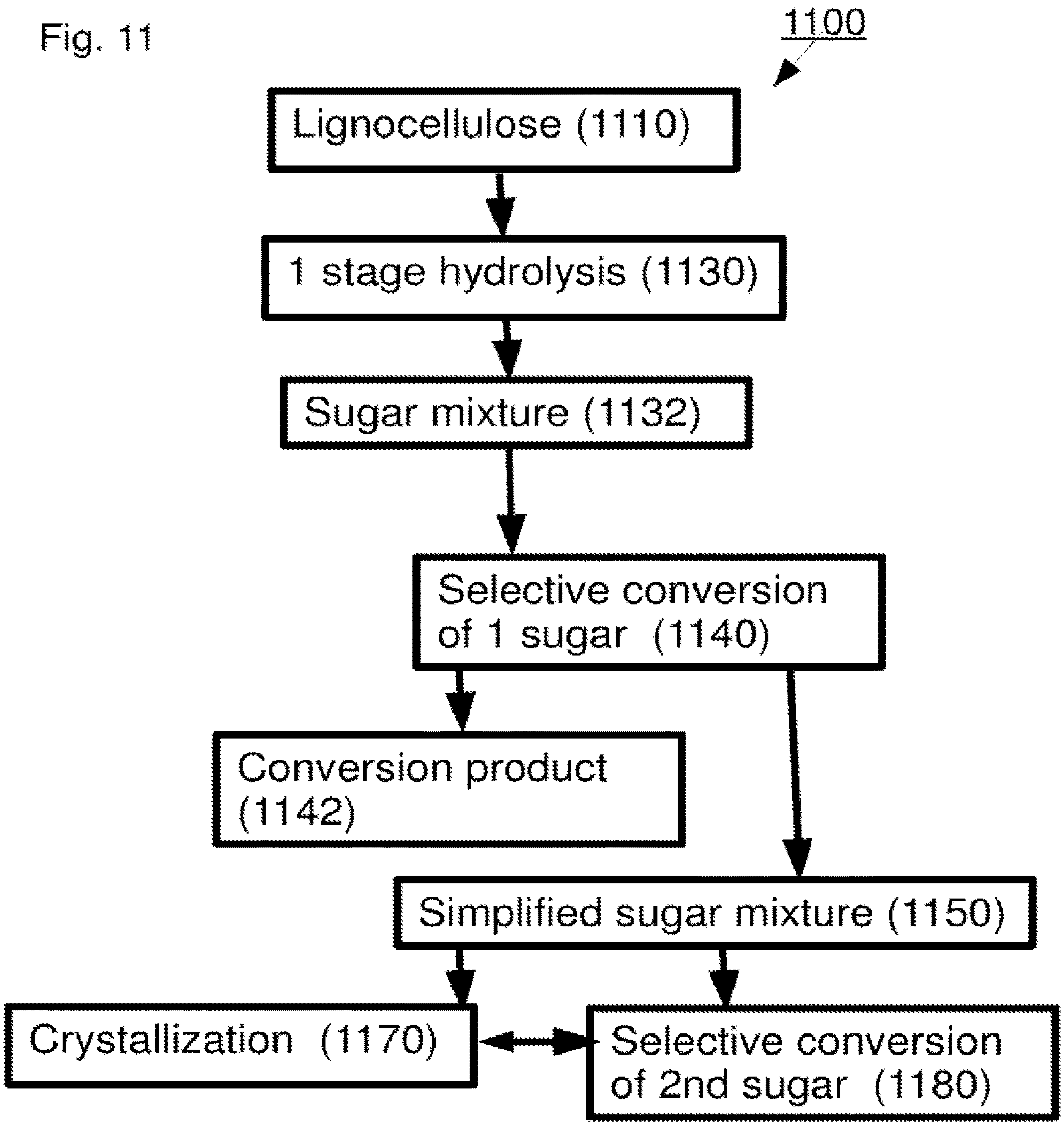

1000
mixture (1010)
1st sugar product (1011)
Modified mixture (1020)
Ultrafiltration (1022)
Concentrated mixture (1024)
Chromatographic separation (1030)
Remaining sugars (1042)
Xylose fraction (1040)
concentration (1050)
Anaerobic fermentation (1044)
crystallization (1060)
Mother liquor (1070)
crystals (1062)
hydrogenation (1124)

Fig. 11


1100
Lignocellulose (1110)
1 stage hydrolysis (1130)
Sugar mixture (1132)
Selective conversion of 1 sugar (1140)
Conversion product (1142)
Simplified sugar mixture (1150)
Crystallization (1170)
Selective conversion of 2nd sugar (1180)

METHODS AND SYSTEMS FOR PROCESSING SUGAR MIXTURES AND RESULTANT COMPOSITIONS

RELATED APPLICATIONS

In accord with the provisions of 35 U.S.C. § 119(a) and/or § 365(b), this application claims priority from:

prior Israeli application IL207945 filed on 2 Sep. 2010 by Robert JANSEN et al. and entitled "Method for the Production of Carbohydrates"; and

prior PCT Application IL11/000424 filed on 1 Jun. 2011 by Robert JANSEN et al. and entitled "Lignin Compositions, Systems and Methods for Producing Lignin and/or HCL"; and

prior PCT application IL11/000509 filed on Jun. 26, 2011 by Aharon EYAL et al. and entitled "Sugar Mixtures and Methods for Production and Use thereof"; and

prior PCT application IL11/000517 filed on Jun. 28, 2011 by Aharon EYAL et al. and entitled "Methods and Systems for Processing a Sucrose Crop and Sugar Mixtures"

prior PCT application US 11/46153 filed on 1 Aug. 2011 by Robert JANSEN et al. and entitled "Methods and Systems for Solvent Purification";

the contents of each of which is fully incorporated herein by reference.

In accord with the provisions of 35 U.S.C. § 119(e) and § 363, this application claims the benefit of:

U.S. 61/529,277 filed on 31 Aug. 2011 by Aharon EYAL et al. and entitled "Methods and Systems for Processing Sugar Mixtures and Resultant Compositions"

the contents of which is fully incorporated herein by reference.

In addition, this application is related to the following applications, each of which is fully incorporated herein by reference:

U.S. 61/483,777 filed on 9 May 2011 by Robert JANSEN et al. and entitled "Hydrolysis Systems and Methods";

U.S. 61/487,319 filed on 18 May 2011 by Robert JANSEN et al. and entitled "Hydrolysis Systems and Methods"; and

U.S. 61/524,839 filed on 18 Aug. 2011 by Robert JANSEN et al. and entitled "Systems and Methods for Sugar Refining".

FIELD OF THE INVENTION

This invention relates to processing of sugars.

BACKGROUND OF THE INVENTION

Plants are composed in large part of lignocellulosic material and smaller amounts of lipophilic materials (often referred to as "extractives") and minerals (i.e. ash).

The lignocellulosic material includes lignin, cellulose and hemicellulose.

Cellulose and hemicellulose are each polymeric saccharides (i.e. polysaccharides) of monomeric saccharides (i.e. monosaccharides). Although cellulose and hemicellulose are carbohydrates in a strict chemical sense, the bond types used to connect the monomeric saccharides, and/or the specific monosaccharides in the polymer, make them less physiologically available than other polymeric carbohydrates such as amylan (starch).

Cellulose is rich in six-carbon sugars (hexoses), such as glucose, mannose and galactose. Hemicellulose includes a significant amount of five-carbon sugars (pentoses), such as xylose and arabinose.

Some of these monosaccharides form a large fraction of the total saccharides (e.g. glucose) in the lignocellulosic material, while others are present in relatively low amounts.

Lignocellulosic material is available in a wide variety of forms. In many cases lignocellulosic material is a by-product or waste product. For example, corn stover is a by-product of the corn industry. Alternatively or additionally, the bagasse remaining after initial extraction of sucrose from sugar cane is primarily lignocellulosic. When lignocellulosic material is the by-product, it is often present in a greater quantity by weight than the primary product, as in the case of corn stover and sugar cane bagasse.

In other cases, the primary product is lignocellulosic (e.g. wood produced from timber).

SUMMARY OF THE INVENTION

A broad aspect of the invention relates to sugar processing. More specifically the various exemplary embodiments of the invention described in this application relate to methods of processing a mixture containing more than one sugar.

As used in this specification and the accompanying claims the term "sugar" indicates a monosaccharide or an oligosaccharide containing at least two monosaccharide sub-units and having a solubility greater than 5% in water at 25 degrees centigrade.

In some exemplary embodiments of the invention, one or more of the sugars in the mixture is provided as a "precursor".

As used in this specification and the accompanying claims a "precursor" of a sugar indicates any molecule that can be transformed to the corresponding sugar in one or two chemical reactions. For example, a monosaccharide or an oligosaccharide can be a precursor of another monosaccharide, of a disaccharide or of a longer polysaccharide. For example, glucose can be a precursor of fructose. Alternatively or additionally, an oligosaccharide (e.g. disaccharide) can be a precursor of a different disaccharide or a longer polysaccharide. Alternatively or additionally, esters or ethers of sugars can be precursors of the corresponding sugars.

One aspect of some embodiments of the invention relates to selectively reacting a first sugar in the presence of a second (different) sugar (or a precursor of the second sugar) to form a product mixture including a product produced from the first sugar followed by separating that product from the mixture. In some exemplary embodiments of the invention, the first sugar is glucose and the product produced from the first sugar is ethanol. Optionally, removal of the product produced from the first sugar can be via distillation.

Alternatively or additionally, according to various exemplary embodiments of the invention the selective reaction includes fermentation via a suitable micro-organism for the first sugar in question. In some exemplary embodiments of the invention, selection of a micro-organism with a specific ability to ferment a desired first sugar contributes to selectivity of the reaction.

In some exemplary embodiments of the invention, the second sugar is present as a sugar per se. The second sugar is optionally removed from the reaction mixture as a sugar. Alternatively or additionally, the second sugar is processed to a product produced from the second sugar. According to various exemplary embodiments of the invention, this processing occurs in the mixture or after removal of the second sugar from the mixture.

In some exemplary embodiments of the invention, the product produced from the second sugar is removed from the mixture. Removal techniques for the product include, but are not limited to crystallization, microfiltration and chromatographic separation. Optionally, the product produced from the second sugar is modified to produce a modified product.

In some exemplary embodiments of the invention, the second sugar is present as a sugar precursor. In some exemplary embodiments of the invention, the second sugar precursor is removed from the reaction mixture as a sugar precursor.

In those exemplary embodiments of the invention in which the second sugar is processed to a product produced from the second sugar, this processing can occur in the mixture or after removal of the second sugar from the mixture.

In some exemplary embodiments of the invention, the product produced from the second sugar is removed from the mixture. Removal techniques for the product include, but are not limited to crystallization, microfiltration and chromatographic separation. Optionally, the product produced from the second sugar is modified to produce a modified product.

Another aspect of some exemplary embodiments of the invention relates to increasing a relative concentration of a second sugar in a mixture by removing a first sugar. In some exemplary embodiments of the invention, removal of the first sugar includes conversion of the first sugar to a first sugar product.

Some exemplary embodiments of the invention, relate to preparation of the mixture. Optionally, this preparation includes hydrolysis of a lignocellulosic substrate. In some exemplary embodiments of the invention, this hydrolysis employs a strong acid, for example HCl or H_2SO_4. According to various exemplary embodiments of the invention the acid is applied to the substrate at a concentration of 30, 32, 34, 36, 38, 40, 42, 44 or 46%, or intermediate or greater percentages, as calculated by wt of acid/[wt of acid+water].

Some exemplary embodiments of the invention relate to further processing of a product of the first sugar and/or a second sugar to a conversion product.

One aspect of some embodiments of the invention relates to selectively removing at least two monomeric sugars from a sugar mixture containing oligomeric sugars and processing at least a portion of the oligomeric sugars to produce additional monomeric sugars. In some exemplary embodiments of the invention, at least one of the two monomeric sugars is converted to a product and the product is removed from the mixture. Alternatively or additionally, at least one of the two monomeric sugars is crystallized and the crystals are removed from the mixture. In some exemplary embodiments of the invention, processing of the oligomeric sugars includes hydrolysis. Optionally, this hydrolysis is in a dilute acid solution. Optionally, the dilute acid solution includes at least 4, optionally at least 6, optionally at least 9%, or intermediate or greater percentages of acid. Optionally, the dilute acid solution includes less than 15, optionally less than 12, optionally less than 11%, or intermediate or lower percentages of acid. In some exemplary embodiments of the invention, the dilute acid solution includes 4 to 15%, optionally 6 to 12%, optionally 9 to 11% acid. In some exemplary embodiments of the invention, HCl is employed for this hydrolysis.

One aspect of some embodiments of the invention relates to fermentation of glucose in a sugar mixture to produce ethanol and use of at least a portion of the produced ethanol in crystallization of a non-glucose sugar from the mixture. According to various exemplary embodiments of the invention the non-glucose sugar can be monomeric or oligomeric (disaccharide; trisacchararide or longer oligomer). In some exemplary embodiments of the invention, two or more rounds of crystallization are conducted to separate a series of different sugars from the mixture.

Another aspect of some embodiments of the invention relates to a system designed and configured to separate sugars from a mixture using a combination of fermentation to produce an alcohol from one sugar followed by crystallization of at least one additional sugar using the alcohol.

It will be appreciated that the various aspects described above relate to the solution of technical problems associated with harvest of minor components of a mixture in an industrial context.

Alternatively or additionally, it will be appreciated that the various aspects described above relate to the solution of technical problems related to re-arrangement of a sequence of monosaccharide units within an oligosaccharide.

Alternatively or additionally, it will be appreciated that the various aspects described above relate to solution of technical problems related to exploitation of multiple components in a sugar mixture.

In some exemplary embodiments of the invention, there is provided a method including: (a) selectively reacting a first sugar in a mixture which includes at least one second sugar to form a product mixture including a product of the first sugar; (b) separating the product of the first sugar from the product mixture; and (c) separating at least one of the at least one second sugar from the product mixture.

In some exemplary embodiments of the invention, there is provided a method including: (a) selectively reacting a first sugar in a mixture which includes at least one second sugar, to form a product mixture including a product of the first sugar; (b) separating the product of the first sugar from the product mixture; and (c) reacting at least one of the at least one second sugar to form a second sugar product.

In some exemplary embodiments of the invention, there is provided a method including: (a) selectively reacting a first sugar in a mixture which includes at least one second sugar precursor, to form a product mixture including a product of the first sugar; (b) separating the product of the first sugar from the product mixture; and (c) reacting at least one of the at least one second sugar precursor to form a second sugar product.

Optionally, the method includes separating at least one of the at least one second sugar from the product mixture.

Optionally, the method includes separating at least one second sugar product from the product mixture.

Optionally, the first sugar includes glucose and wherein the selectively reacting includes fermenting.

Optionally, the at least one second sugar precursor includes a pentose.

Optionally, the at least one second sugar includes a pentose.

Optionally, the pentose is selected from the group consisting of xylose, xylulose, lyxose, ribulose and arabinose.

Optionally, the at least one second sugar includes a disaccharide.

Optionally, the at least one second sugar precursor includes a disaccharide.

Optionally, the disaccharide is selected from the group consisting of trehalose, gentiobiose, kojibiose, nigerose, sophorose and laminarobiose.

Optionally, the second sugar is xylose.

Optionally, the method includes reacting the second sugar to form a second sugar product.

Optionally, the method includes reacting the second sugar precursor to form a second sugar product.

Optionally, the second sugar is xylose and the second sugar product is selected from xylitol and a rumen bypass protein.

Optionally, the weight ratio between the second sugar to the first sugar prior to the selectively reacting is R1;

the weight ratio between the second sugar to the first sugar in the product mixture is R2; and

the ratio of R2 to R1 is greater than 5.

Optionally, the weight ratio between the second sugar precursor to the first sugar prior to the selectively reacting is R1;

the weight ratio between the second sugar precursor to the first sugar in the product mixture is R2; and

the ratio of R2 to R1 is greater than 5.

Optionally, the total weight of the second sugar includes at least 50% of the total sugars in the product mixture.

Optionally, the total weight of the second sugar precursor is equal to at least 50% of the total sugars in the product mixture.

Optionally, the product of the first sugar is selected from the group consisting of ethanol, higher alcohols, organic acids and organic acid ester of 3 to 22 carbon atoms, amino acids, yeast and proteins.

Optionally, the separating includes at least one of distillation, membrane filtration, solvent extraction and chromatographic separation.

Optionally, the product of the first sugar has an atmospheric-pressure boiling point of less than 100° C.

Optionally, the product of the first sugar forms an azeotrope with water.

In some exemplary embodiments of the invention, there is provided a method including: (a) providing a mixture including a first sugar and at least one second sugar precursor; (b) selectively reacting the first sugar to form a product mixture including a product of the first sugar; (c) selectively reacting the precursor to form the second sugar; and (d) separating the product of the first sugar.

Optionally, the method includes separating at least one of the at least one second sugar precursor from the product mixture.

Optionally, selectively reacting the precursor to form the second sugar occurs after separating the product of the first sugar.

Optionally, separating the product of the first sugar from the second sugar includes separating each of the product of the first sugar and the second sugar from the product mixture.

Optionally, separating the product of the first sugar is followed by separating the second sugar precursor.

Optionally, separating the product of the first sugar is followed by selectively reacting the precursor to form the second sugar.

Optionally, selectively reacting the precursor includes acid catalysis.

Optionally, selectively reacting the precursor includes enzymatic catalysis.

Optionally, selectively reacting the first sugar includes fermentation.

Optionally, selectively reacting the precursor includes hydrolysis.

Optionally, selectively reacting the precursor includes transglucosidation.

Optionally, selectively reacting the precursor, includes oligomerization.

Optionally, the method includes reacting the second sugar to form a second sugar product.

Optionally, the method includes preparing the mixture.

Optionally, the preparing includes:

providing a lignocellulosic material feed;

hydrolyzing the lignocellulosic material feed to form a hydrolyzate including at least one first sugar and at least one of at least one second sugar and at least one second sugar precursor.

Optionally, the method includes de-acidifying the hydrolyzate.

Optionally, the hydrolyzing is performed in a counter-current mode.

Optionally, the lignocellulosic material feed includes at least 5% hemicellulose.

Optionally, the hydrolyzing employs a hydrolysis medium with a wt/wt ratio of HCl to (HCl+water) of at least 0.35.

Optionally, the de-acidifying includes selective extraction of HCl with an alcohol.

Optionally, an amount of at least one of the at least one second sugars in the mixture, optionally present as a precursor, is at least 85% of a theoretical yield of the same second sugar in the lignocellulosic material feed.

Optionally, the combined concentration of the second sugar and the second sugar precursor in the mixture is C1; wherein the combined concentration of the second sugar and the second sugar precursor in the product mixture after removal of the first sugar product is C2 and C2/C1 is greater than 1.5.

In some exemplary embodiments of the invention, there is provided a method including: (a) providing a fermentor; and (b) fermenting a medium including a second sugar according as described above in the fermentor to produce a conversion product.

In some exemplary embodiments of the invention, there is provided a method including: (a) providing an input stream including at least one member of the group consisting of:

the second sugars as described above; and

the product of the first sugar as described above; and (b) converting at least a portion of the input stream to produce a conversion product.

Optionally, the conversion product includes at least one member selected from the group consisting of alcohols, carboxylic acids, amino acids, monomers for the polymer industry and proteins.

Optionally, the method includes processing the conversion product to produce a consumer product selected from the group consisting of detergent, polyethylene-based products, polypropylene-based products, polyolefin-based products, polylactic acid (polylactide)-based products, polyhydroxyalkanoate-based products and polyacrylic-based products.

Optionally, the detergent includes a sugar-based surfactant, a fatty acid-based surfactant, a fatty alcohol-based surfactant, or a cell-culture derived enzyme.

Optionally, the polyacrylic-based product is selected from plastics, floor polishes, carpets, paints, coatings, adhesives, dispersions, flocculants, elastomers, acrylic glass, absorbent articles, incontinence pads, sanitary napkins, feminine hygiene products, and diapers.

Optionally, the polyolefin-based products are selected from milk jugs, detergent bottles, margarine tubs, garbage containers, water pipes, absorbent articles, diapers, nonwovens, high density polyethylene (HDPE) toys and HDPE detergent packagings.

Optionally, the polypropylene based products are selected from absorbent articles, diapers and non wovens.

Optionally, the polylactic acid based products are selected from packaging of agriculture products and of dairy products, plastic bottles, biodegradable products and disposables.

Optionally, the polyhydroxyalkanoate based products are selected from packaging of agriculture products, plastic bottles, coated papers, molded or extruded articles, feminine hygiene products, tampon applicators, absorbent articles, disposable nonwovens and wipes, medical surgical garments, adhesives, elastomers, films, coatings, aqueous dispersants, fibers, intermediates of pharmaceuticals and binders.

Optionally, the conversion product includes at least one member of the group consisting of ethanol, butanol, isobutanol, a fatty acid, a fatty acid ester, a fatty alcohol and biodiesel.

Optionally, the method includes processing of the conversion product to produce at least one product selected from the group consisting of an isobutene condensation product, jet fuel, gasoline, gasohol, diesel fuel, drop-in fuel, a diesel fuel additive, and a precursor thereof.

Optionally, the gasahol is ethanol-enriched gasoline or butanol-enriched gasoline.

Optionally, the product is selected from the group consisting of diesel fuel, gasoline, jet fuel and drop-in fuels.

In some exemplary embodiments of the invention, there is provided a consumer product, a precursor of a consumer product, or an ingredient of a consumer product produced from a conversion product as described above.

In some exemplary embodiments of the invention, there is provided a consumer product, a precursor of a consumer product, or an ingredient of a consumer product including at least one conversion product produced by a method as described above, wherein the conversion product is selected from carboxylic and fatty acids, dicarboxylic acids, hydroxylcarboxylic acids, hydroxyl di-carboxylic acids, hydroxyl-fatty acids, methylglyoxal, mono-, di-, or poly-alcohols, alkanes, alkenes, aromatics, aldehydes, ketones, esters, biopolymers, proteins, peptides, amino acids, vitamins, antibiotics, and pharmaceuticals.

Optionally, the consumer product is ethanol-enriched gasoline, jet fuel, or biodiesel.

Optionally, the consumer product, a precursor of a consumer product, or an ingredient of a consumer product as described above, wherein the consumer product has a ratio of carbon-14 to carbon-12 of at least about 2.0×10^{-13}.

In some exemplary embodiments of the invention, relate to a consumer product including an ingredient as described above, and an additional ingredient produced from a raw material other than a lignocellulosic material.

Optionally, the conversion product includes xylitol.

Optionally, the method includes incorporating the xylitol into an edible product.

Optionally, the conversion product includes rumen bypass protein.

Optionally, the method includes incorporating the rumen bypass protein into a livestock feed.

Optionally, the ingredient and the additional ingredient produced from a raw material other than a lignocellulosic material are essentially of the same chemical composition.

Optionally, the consumer product as described above includes a marker molecule at a concentration of at least 100 ppb.

According to various exemplary embodiments of the invention the marker molecule is selected from the group consisting of furfural, hydroxy-methyl furfural, products of furfural or hydroxy-methylfurfural condensation, color compounds formed on heating a sugar, levulinic acid, acetic acid, methanol, galacturonic acid, an alcohol of more than four carbon atoms betaine, amino acids, proteins phosphate and glycerol.

In some exemplary embodiments of the invention, there is provided a method including: (a) selectively reacting a first sugar in an initial mixture which includes at least one oligosaccharide to form a product mixture including a product of the first sugar; (b) producing an oligosaccharide rich sugar fraction with a ratio of at least one of the at least one oligosaccharide to a total sugar concentration greater than a same ratio in the product mixture; and (c) hydrolyzing the oligosaccharide rich sugar fraction to produce monomeric sugars.

Optionally, the first sugar is a monomeric sugar.

Optionally, the initial mixture includes at least one additional monomeric sugar.

In some exemplary embodiments of the invention, there is provided a method including: (a) selectively reacting a first sugar in an initial mixture which includes a first sugar and at least one oligosaccharide to form a product mixture including a product of the first sugar; (b) separating the product of the first sugar from the product mixture; and (c) hydrolyzing the oligosaccharide to produce additional first sugar.

Optionally, the initial mixture includes a second sugar.

Optionally, the method includes separating the second sugar.

Optionally, the method includes separating the product of the first sugar from the product mixture.

Optionally, the method includes separating at least one monomeric sugar from the product mixture.

Optionally, the selectively reacting produces an alcohol.

Optionally, the initial mixture includes a second sugar, and includes use of the alcohol to aid in crystallization of the second sugar.

Optionally, the method includes: distilling the alcohol from the product mixture; and re-introducing the alcohol during the crystallization.

Optionally, the method includes crystallizing the second sugar; and distilling the alcohol from the product mixture.

Optionally, the producing an oligomer rich sugar fraction includes crystallization of at least one of the at least one oligosaccharide from the product mixture.

Optionally, the selectively reacting the first sugar produces an alcohol.

Optionally, the method includes use of the alcohol to aid in the crystallization.

In some exemplary embodiments of the invention, there is provided a method including: (a) fermenting glucose in a portion of an initial mixture which includes at least one additional monomeric sugar and at least one oligosaccharide to form a product mixture including ethanol; and (b) using the ethanol to aid in crystallization of at least one non-glucose sugar in the product mixture.

Optionally, crystallization of at least one non-glucose sugar produces crystals including primarily at least one of the at least one additional monomeric sugar and an oligosaccharide enriched mother liquor.

Optionally, the method includes hydrolyzing the oligosaccharide enriched mother liquor to produce additional monomeric sugars.

Optionally, crystallization of at least one non-glucose sugar produces crystals including primarily at least one of the at least one oligosaccharide and a monomeric sugar enriched mother liquor.

Optionally, the method includes crystallizing at least one monomeric sugar from the monomeric sugar enriched mother liquor.

Optionally, the method includes using ethanol to aid in crystallization of the at least one monomeric sugar.

In some exemplary embodiments of the invention, there is provided a system including: (a) a fermentor adapted to deliver a stream of spent media to a separation unit; (b) the separation unit adapted to separate solids from the spent media and deliver a supernatant stream; (c) a still adapted to distill an alcohol from the supernatant stream to produce a modified supernatant; (d) a primary crystallization module adapted to receive at least a portion of the alcohol from the distillation unit and crystallize at least one sugar from the modified supernatant to produce a mother liquor.

Optionally, the system includes a secondary crystallization module adapted to receive at least a portion of the alcohol from the distillation unit and crystallize at least one additional sugar from the mother liquor to produce a spent mother liquor.

Optionally, the system includes an alcohol recovery module adapted to distill the alcohol from at least one of the mother liquor and the spent mother liquor.

Optionally, the system includes a hydrolysis module adapted to:

receive a material selected from the group consisting of: crystals produced by the primary crystallization module; the mother liquor; crystals produced by the secondary crystallization module and the spent mother liquor; and

hydrolyze the received material to produce additional monomeric sugars.

Optionally, the system includes: a recycling module adapted to deliver the additional monomeric sugars to the fermentor.

Optionally, the system includes at least one pump to control flows among and between components of the system.

Optionally, the system includes a controller adapted to control at least one of the at least one pumps.

Optionally, the system includes at least one detector configured to provide data pertaining to at least one system parameter to the controller, wherein the controller is responsive to the data.

In some exemplary embodiments of the invention, there is provided a sugar composition including:

(a) at least 25% xylose by weight relative to total sugar concentration;

(b) at least one alpha-bonded di-glucose; and

(c) at least one beta-bonded di-glucose.

Optionally, the alpha-bonded di-glucose includes at least one member of the group consisting of maltose, isomaltose and trehalose.

Optionally, the beta-bonded di-glucose includes at least one member selected from the group consisting of gentiobiose, sophorose and cellobiose.

Optionally, the composition includes at least 40% total sugars.

Optionally, the composition is provided as a solution.

Optionally, the composition includes less than 90% xylose of total sugars on a weight basis.

Optionally, the composition includes glucose between 0.001% and 5% of total sugars on a weight basis.

Optionally, the composition includes at least 0.001% arabinose of total sugars on a weight basis.

Optionally, the composition includes at least 0.001% non-volatile fermentation product on a weight basis.

In some exemplary embodiments of the invention, there is provided a sugar composition including (by weight relative to total sugar concentration):

(a) at least 60% xylose;

(b) at least 100 PPB of a marker molecule; and

(c) 0.001% to 10% oligosaccharides.

Optionally, the marker molecule is selected from the group consisting of furfural, hydroxy-methyl furfural, products of furfural or hydroxy-methylfurfural condensation, color compounds formed on heating a sugar, levulinic acid, acetic acid, methanol, galacturonic acid, an alcohol of more than four carbon atoms, betaine, amino acids, proteins phosphate and glycerol.

Optionally, the composition includes at least two marker molecules.

Optionally, the composition includes at least three marker molecules.

Optionally, the composition includes at least one fermentation residue.

Optionally, the at least one fermentation residue is a component of an ingredient selected from the group consisting of sugar molasses, yeast extract and corn steep liquor.

Optionally, the composition includes at least two fermentation residues.

Optionally, the composition includes at least three fermentation residues.

Optionally, the composition includes glucose between 0.001% and 5% of total sugars on a weight basis.

Optionally, the composition includes at least 0.001% arabinose of total sugars on a weight basis.

Optionally, the oligosaccharides include at least one member of the group consisting of maltose, isomaltose and trehalose.

Optionally, the oligosaccharides include at least one member selected from the group consisting of gentiobiose, sophorose and cellobiose.

Optionally, the composition includes at least 0.001% non-volatile fermentation product on a weight basis.

Optionally, a concentration of the marker molecule does not exceed 0.5%.

Optionally, the composition includes at least 60% total sugars.

Optionally, the composition includes at least one sugar selected from the group consisting of mannose, galactose and arabinose.

Optionally, the composition includes at least 3% mannose relative to total monosaccharides by weight.

Optionally, the composition includes at least 5% galactose relative to total monosaccharides by weight.

Optionally, the composition includes at least 2% arabinose relative to total monosaccharides by weight.

In some exemplary embodiments of the invention, there is provided a sugar composition including: (a) at least one of alpha-bonded di-glucose, beta-bonded di-glucose and arabinose; (b) 0.01%-20% xylose by weight relative to total sugar concentration; and (c) at least 100 PPB of a marker molecule.

Optionally, the composition is provided as a solution.

Optionally, the composition includes glucose between 0.001% and 5% (3, 1) of total sugars on a weight basis.

Optionally, the composition includes at least 0.001% non-volatile fermentation product on a weight basis.

Optionally, the alpha-bonded di-glucose includes at least one member of the group consisting of maltose, isomaltose and trehalose.

Optionally, the beta-bonded di-glucose includes at least one member selected from the group consisting of gentiobiose, sophorose and cellobiose.

Optionally, the composition includes at least 40% total sugars.

Optionally, the marker molecule is selected from the group consisting of furfural, hydroxy-methyl furfural, products of furfural or hydroxy-methylfurfural condensation, color compounds formed on heating a sugar, levulinic acid, acetic acid, methanol, galacturonic acid, an alcohol of more than four carbon atoms, betaine, amino acids, proteins phosphate and glycerol.

Optionally, the composition includes at least two marker molecules.

Optionally, the composition includes at least three marker molecules.

Optionally, the composition includes at least one fermentation residue.

Optionally, the at least one fermentation residue is a component of an ingredient selected from the group consisting of sugar molasses, yeast extract and corn steep liquor.

Optionally, a concentration of the marker molecule does not exceed 0.5%.

Optionally, the composition includes a sugar selected from the group consisting of mannose and galactose.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although suitable methods and materials are described below, methods and materials similar or equivalent to those described herein can be used in the practice of the various embodiments of the invention. In case of conflict, the patent specification, including definitions, will control. All materials, methods, and examples are illustrative only and are not intended to be limiting.

As used herein, the terms "comprising" and "including" or grammatical variants thereof are to be taken as specifying inclusion of the stated features, integers, actions or components without precluding the addition of one or more additional features, integers, actions, components or groups thereof. This term is broader than, and includes the terms "consisting of" and "consisting essentially of" as defined by the Manual of Patent Examination Procedure of the United States Patent and Trademark Office.

The term "method" refers to manners, means, techniques and procedures for accomplishing a given task including, but not limited to, those manners, means, techniques and procedures either known to, or readily developed from, known manners, means, techniques and procedures by practitioners of chemistry and/or engineering.

Percentages (%) of chemicals typically supplied as powders or crystals (e.g. sugars) are W/W (weight per weight) unless otherwise indicated. Percentages (%) of chemicals typically supplied as liquids (e.g. alcohols) are W/W (weight per weight) unless otherwise indicated.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to understand the invention and to see how it may be carried out in practice, embodiments will now be described, by way of non-limiting example only, with reference to the accompanying figures. In the figures, identical and similar structures, elements or parts thereof that appear in more than one figure are generally labeled with the same or similar references in the figures in which they appear. Dimensions of components and features shown in the figures are chosen primarily for convenience and clarity of presentation and are not necessarily to scale.

In the attached figures:

FIG. **1** is a schematic representation of a hydrolysis system which can be used to produce a sugar mixture according to some exemplary embodiments of the invention;

FIG. **2***a* is a simplified flow scheme depicting events associated with practice of exemplary methods according to some embodiments of the invention;

FIG. **2***b* is a simplified flow scheme depicting events associated with practice of exemplary methods according to some embodiments of the invention;

FIG. **2***c* is a simplified flow scheme depicting events associated with practice of exemplary methods according to some embodiments of the invention;

FIG. **3** is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

FIG. **4** is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

FIG. **5** is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

FIG. **6***a* is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

FIG. **6***b* is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

FIG. **7***a* is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

FIG. **7***b* is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

FIG. **8***a* is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

FIG. **8***b* is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

FIG. **8***c* is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

FIG. **9** is a schematic representation of an exemplary system according to some embodiments of the invention;

FIG. **10** is a simplified flow diagram of exemplary methods according to some embodiments of the invention; and

FIG. **11** is a logic hierarchy illustrating approaches to separating products of value from lignocelluloses.

DETAILED DESCRIPTION OF EMBODIMENTS

Embodiments of the invention relate to systems and methods for processing mixtures of sugars as well as to modified sugar mixtures found at various stages during this processing. In many exemplary embodiments of the invention, the mixture contains two or more monomeric sugars (e.g. glucose and xylose) and one or more disaccharides or longer oligosaccharide sugars.

Specifically, some embodiments of the invention can be used to process hydrolyzates of lignocellulosic substrates. Optionally, these hydrolyzates result from acid hydrolysis (e.g. with concentrated HCl).

The principles and operation of a system and/or method according to exemplary embodiments of the invention may be better understood with reference to the drawings and accompanying descriptions.

Before explaining at least one embodiment of the invention in detail, it is to be understood that the invention is not limited in its application to the details set forth in the following description or exemplified by the Examples. The invention is capable of other embodiments or of being practiced or carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein is for the purpose of description and should not be regarded as limiting.

Exemplary Source of Sugar Mixtures

FIG. **1** is a simplified schematic diagram of a system for acid hydrolysis of a lignocellulosic substrate indicated generally as **100**. Depicted system **100** includes a main hydrolysis reactor **110** adapted to receive a lignocellulosic substrate input **112**. Optionally, substrate **112** is provided as wood chips, although any "woody material" can be used instead of wood. Additional exemplary woody materials include, but are not limited to, sugar cane bagasse, sugar beets and/or their cossettes, corn stover, post harvest plants (e.g. cotton, soybean or rapeseed), switchgrass and broomgrass.

In the depicted exemplary system, substrate **112** is brought into contact with a concentrated HCl solution in reactor **110** and hemicellulose and/or cellulose in the substrate are hydrolyzed to produce a mixture of soluble sugars and residual lignin. These materials are collected separately as lignin stream **120** and sugar mixture **130**, each of which contains a large amount of HCl.

Since the acid acts as a catalyst, it is not consumed in the process. In addition, residual acid content of the product and the co-products should be low in order to enable their use. Acid recovery from the hydrolyzate should be conducted under conditions minimizing thermal degradation. Alternatively or additionally, the high concentration of monomeric sugars in the presence of the HCl catalyst can cause re-oligomerization. Cellulose in substrate **112** typically contains primarily beta bonds between the saccharide sub-units of the polymer chain. Dimers and longer oligosaccharides resulting from re-oligomerization can contain alpha bonds.

Details of exemplary hydrolysis methods and systems are described in detail in U.S. provisional applications 61/483,777 and 61/487,319; each of which is fully incorporated herein by reference. According to various exemplary embodiments of the invention the way in which hydrolysis is conducted in reactor **110** contributes to the composition of sugar mixture **130** and/or lignin stream **120**. Contribution to the composition of sugar mixture **130** and/or lignin stream **120** may be, for example, a reduction in the amount of sugar degradation products in the mixture and/or an increase in yield of intact pentoses such as xylose.

Sugar mixture **130** is processed to remove HCl and/or adjust the mixture to achieve one or more desired ratios of mixture components (e.g. disaccharides and/or monosaccharides). This processing is conducted in a sugar refining module, designated here generically as **201**.

Optionally, additional sugar mixture is recovered from lignin stream **120** as described in co-pending PCT application IL11/000424 which is fully incorporated herein by reference. In some exemplary embodiments of the invention, this additional sugar mixture is routed to refining module **201**. According to various exemplary embodiments of the invention this additional sugar mixture increases a total sugar yield and/or changes a composition of the mixture.

In depicted system **100**, refining module **201** employs a flow of organic solvent **155** (solid arrows) to extract HCl **140** (dashed arrows) from sugar mixture **130**.

De-acidified sugars **230** are the primary product of refining module **201**. Module **201** also produces a stream of HCl **140** mixed with solvent **155** (depicted as parallel dashed and solid arrows respectively for clarity) which is routed to a solvent/HCl recovery module **150**. Recovery module **150** separates HCl **140** from solvent **155**. In some exemplary embodiments of the invention, separation is by distillation. HCl **140** is recycled to hydrolysis reactor **110** and solvent **155** is recycled to refining module **201**.

De-acidified sugars **230** are present as a mixture. Various components of the mixture can be harvested and/or converted as described hereinbelow. Each strategy for harvest and/or conversion of specific sugars and/or sugar products represents an exemplary embodiment of the invention. In some cases, implementation of specific embodiments will be influenced by an initial composition of sugar mixture **230**. In many cases, sugar mixture **230** will contain glucose as a primary component since glucose is a primary component of lignocellulosic substrate **112**. Alternatively or additionally, in many cases, sugar mixture **230** will contain a significant amount of xylose since xylose is typically the most prevalent saccharide component of hemicellulose in lignocellulosic substrate **112**.

Although HCl hydrolysis of substrate **112** is described by way of example, sugar mixtures resulting from other processes are also amenable to use in various exemplary embodiments of the invention. These other processes include any procedure which converts a large portion of the biomass in substrate **112** to soluble sugars. Such procedures include, but are not limited to, enzymatic hydrolysis, hydrolysis with other acids (e.g. H_2SO_4) and hydrolysis with "reactive fluids" (e.g. super critical or near critical water) as described in WO 2010/009343; which is fully incorporated herein by reference.

Process Overview

FIGS. **2***a*, **2***b* and **2***c* are simplified flow schemes depicting events associated with practice of exemplary methods according to various embodiments of the invention.

FIG. **2***a* is a flow scheme indicated generally as scheme **200** depicting an exemplary sugar mixture **230** (FIG. **1**). For simplicity, mixture **230** is depicted as containing a first sugar **231** and a second sugar **232** which is optionally present (at least in part) as a precursor **233**. In actuality, mixture **230** typically contains a large number of different sugars, which are not depicted. Each of these different sugars could potentially be treated as a first sugar or a second sugar.

According to scheme **200**, mixture **230** is subjected to a selective reaction **240** to produce a product mixture **250**. As a result of reaction **240**, product mixture **250** includes a product **251** of the first sugar. By way of example, if the first sugar is glucose reaction **240** can be a fermentation reaction (e.g. with yeast or another microorganism capable of using glucose as a substrate) and product **251** can be ethanol and/or yeast. In some exemplary embodiments of the invention, first sugar **231** is substantially completely converted to product **251**.

According to depicted flow scheme **200**, product **251** is separated **260** from 2^{nd} sugar **232** at this stage. Continuing with the example begun above, if product **251** includes ethanol, separation **260** can be by distillation. Alternatively or additionally, if product **251** includes yeast, separation can be via filtration and/or centrifugation. Second sugar **232**, optionally as precursor **233** is depicted here alone for clarity but will often be present as part of a mixture similar to mixture **250** except that it has no first sugar product **251**.

FIG. **2***b* is a flow scheme indicated generally as scheme **202** depicting an additional processing of first sugar product **251**. According to flow scheme **202**, product **251** is subjected to an additional reaction **272**. Reaction **272** can be biological or chemical. Since product **251** is provided in isolation, the specificity of reaction **272** is assured. The result of reaction **272** is a modified product **282** of first sugar product **251**. Continuing the example begun above, if product **251** is ethanol, modified product **282** may be, for example, ethylene.

According to flow scheme **202**, modified product **282** is next subjected to a manufacturing process **292** to produce a manufactured product **293**. For example, process **293** could include polymerization of ethylene to polyethylene and formation of a film as manufactured product **293**. Optionally, manufactured product **293** could be converted to one or more consumer products **295**. In the case of polyethylene, consumer products **295** might include one or more of packaging materials, carrier bags and trash-bags.

It is stressed that the flow scheme of FIGS. **2***a* and **2***b* is very versatile, even if only one first sugar is considered. For example, if first sugar **231** is glucose it can be subject to selective reaction **240** in the form of homolactic acid fermentation to produce lactic acid as product **251**. In this case, reaction **272** might include polymerization as part of manufacturing process **292** to produce a manufactured product **293** in the form of polylactide (PLA). PLA can be used in a wide variety of consumer products **295** including, but not limited to, woven fabrics with improved ironability, microwavable trays, sutures, stents, dialysis media, drug delivery devices, bioplastics, compost bags, food packaging, disposable tableware, non woven textiles, upholstery, disposable garments, awnings, feminine hygiene products, and diapers.

FIG. **2***c* is a flow scheme indicated generally as scheme **204** depicting additional processing of second sugar **232** and/or second sugar precursor **233**. According to various exemplary embodiments of the invention, portions, optionally all of scheme **204** can be conducted before or after separation **260**.

In those exemplary embodiments of the invention, in which second sugar **232** is initially provided as precursor **233**, there are two possibilities for scheme **204**.

According to the first depicted possibility, 2^{nd} sugar **232** is realized **234** from precursor **233**.

According to the second possibility, precursor **233** is converted **275** directly to product **284** of second sugar **232**.

As used in this specification and the accompanying claims the term "realization" indicates a reaction which has a desired sugar as a product.

Realization **234** can include, for example, a chemical reaction (e.g. hydrolysis, oligomerization) and/or an enzymatic reaction (e.g. transglucosidation, oligomerization). When realization **234** is conducted, 2^{nd} sugar **232** is then reacted **274** to produce product **284** of second sugar **232**.

Various ways to accomplish realization **234** and/or reaction **274** and/or conversion **275** are described below.

According to depicted exemplary scheme **204**, product **284** is subjected to a manufacturing process **294** to produce a manufactured product **296** which can optionally be incorporated into one or more consumer products **298**.

For example, if second sugar **232** is xylose, realization **232** can optionally include release of xylose from an oligomeric precursor **233** containing xylose. Optionally, reaction **274** could include hydrogenation to produce xylitol as product **284**. According to this exemplary embodiment, manufacturing process **294** might include concentration to produce a product that is 65, optionally 70, optionally 75, optionally 80, optionally 85% or intermediate or greater percentages of total sugars by weight. Optionally, these sugars could be 65, optionally 70, optionally 75, optionally 80, optionally 85% or intermediate or greater percentages of xylose. Optionally, manufacturing process **294** includes crystallization to produce crystals that are 65, optionally 70, optionally 75, optionally 80, optionally 85% or intermediate or greater percentages of xylose as manufactured product **296**. In some exemplary embodiments of the invention, these crystals are incorporated into edible products (e.g. chewing gum and/or candy) which serve as consumer products **298**.

Exemplary Realization and/or Reaction and/or Direct Conversion

In some exemplary embodiments of the invention, precursor **233** can be an oligosaccharide comprising second sugar **232** (e.g. if second sugar **232** is xylose, precursor **233** can be a xylose-comprising disaccharide or gentiobiose-comprising trisaccharide). In other exemplary embodiments of the invention, second sugar **232** is a disaccharide and/or precursor **233** includes at least two sugars, each of which includes a component of second sugar **232**, e.g. as in the case where second sugar **232** is gentiobiose and the precursor includes maltose and/or isomaltose.

According to various exemplary embodiments of the invention realization **234** and/or reaction **274** and/or conversion **275** can each independently include hydrolysis and/or oligomerization, and/or transglucosidation. As used in this specification and the accompanying claims the term "oligomerization" means combining monosaccharides and/or oligosaccharides to form an oligosaccharide of a higher degree of polymerization (e.g. combining two glucose molecules to form sophorose).

As used in this specification and the accompanying claims the term "transglucosidation" means transfer of at least one carbohydrate between oligosaccharides, e.g. as in

A-A+B-B ➔ 2A-B; or

A-A+B-B ➔ A-A-B+B

Such reacting of the precursor may comprise a combination, e.g. of hydrolysis followed by oligomerization, as in

A-x-A ➔ 2A

2A ➔ A-y-A

where A-x-A and A-y-A are disaccharides composed of the same monosaccharides, but bound by a different bond, e.g. cellobiose and gentiobiose.

Alternatively or additionally, realization **234** and/or reaction **274** and/or conversion **275** can each independently include acid catalysis and/or enzymatic catalysis. Optionally, precursor **233** is catalyzed by HCl. Optionally, temperature influences kinetics of such catalysis. Optionally, the catalysis is enzymatically catalyzed. According to various exemplary embodiments of the invention enzymes such as alpha-glucosidase and/or beta-glucosidase and/or transglucosidases can be employed for this purpose. Optionally, enzymatic catalysis includes fermentation.

According to various exemplary embodiments of the invention realization **234** and/or reaction **274** and/or conversion **275** can each independently include simulated moving bed hydrolysis, sequential simulated moving bed hydrolysis, and ion exchange ISEP® and/or CSEP® (Calgon Carbon Corporation; Pittsburgh, Pa.; USA).

First Exemplary Method

FIG. **3** is a simplified flow diagram of an exemplary method for producing value from at least two sugars from within a complex mixture of sugars, indicated generally as **300**. Depicted exemplary method **300**, includes selectively reacting **310** a first sugar in an initial mixture which includes at least one second sugar and/or at least one second sugar precursor, to form a product mixture **320** including a product of the first sugar and separating **330** the product of the first sugar from product mixture **320**.

Optionally, the first sugar can be glucose; selective reaction **310** can be fermentation with a micro-organism with a strong preference for glucose, to produce ethanol as a product. In this case, separation **330** can be, for example, by distillation of ethanol from product mixture **320**.

Alternatively or additionally, the second sugar can be a pentose.

In some exemplary embodiments of the invention, method **300** includes separating **340** at least one of the at least one second sugar from product mixture **320**.

Optionally, at least one of said at least one second sugar is at least partly present as a second sugar precursor. In some exemplary embodiments of the invention, method **300** includes separating **342** at least one of the at least one second sugar precursor from product mixture **320**. According to these exemplary embodiments of method **300**, the method includes reacting **350** the precursor to produce the second sugar.

In other exemplary embodiments of the invention, reacting of the precursor to produce the second sugar occurs in product mixture **320** or in the initial mixture prior to selectively reacting **310** (not depicted).

According to various exemplary embodiments of the invention reacting **350** the precursor includes acid catalysis and/or enzymatic catalysis.

Optionally, the second sugar is reacted to form a second sugar product (not depicted). Alternatively a second sugar precursor can be reacted to form a second sugar product directly without forming the second sugar as an intermediate (not depicted).

In those exemplary embodiments of the invention where the second sugar is xylose the second sugar product can be, for example, xylitol or a rumen bypass protein. Conversion of xylose to xylitol can be, for example, via hydrogenation.

Exemplary Ratios

Method **300** can be conducted with a high degree of efficiency. This efficiency can be expressed as one or more ratios. Optionally, such ratios can be used to characterize additional exemplary embodiments of the invention.

For example, if a weight ratio between the total amount of (second sugar and second sugar precursor) to the first sugar prior to selectively reacting **310** is defined as R1 and a ratio between the total amount of (second sugar and second sugar precursor) to the first sugar in product mixture **320** is defined as R2: in some exemplary embodiments of the invention the ratio of R2 to R1 is optionally greater than 4, optionally greater than 5, optionally greater than 6, optionally greater than 7, optionally greater than 10 or intermediate or larger numbers.

Alternatively or additionally, in some exemplary embodiments of the invention, a total weight of (the second sugar and the second sugar precursor) is at least 40; optionally 50; optionally 60; optionally 70% or intermediate or greater percentages of the total sugars in product mixture **320** by weight.

Exemplary Second Sugars

In some exemplary embodiments of the invention, the second sugar includes a pentose.

Exemplary pentoses include, but are not limited to xylose and/or xylulose and/or lyxose and/or ribulose and/or arabinose. Optionally the second sugar is xylose.

In some exemplary embodiments of the invention, the at least one second sugar includes a disaccharide. Optionally, the disaccharide includes trehalose and/or gentiobiose and/or kojibiose and/or nigerose and/or sophorose and laminaribiose.

Exemplary First Sugar Products

In some exemplary embodiments of the invention, the first sugar product has an atmospheric-pressure boiling point of less than 100° C. Alternatively or additionally, in some exemplary embodiments of the invention, the first sugar product forms an azeotrope with water.

According to various exemplary embodiments of the invention the first sugar product includes an alcohol (e.g. ethanol or a higher alcohol) and/or an organic acid and/or an organic acid ester of 3 to 22 carbon atoms and/or an amino acid and/or yeast and/or a protein. Optionally, a single first sugar (e.g. glucose) can yield more than one first sugar product. For example, yeast and ethanol are two separate products produced when glucose serves as the first sugar and selective reaction **310** includes fermentation with yeast. According to various exemplary embodiments of the invention yeast and ethanol can be removed by different methods (e.g. centrifugation and distillation respectively) and/or at different points in the process (e.g. yeast may be removed prior to separation **340** and/or **342** and ethanol may be removed after separation **340** and/or **342**).

Exemplary Separation Methods

According to various exemplary embodiments of the invention each of separation **330**, separation **340** and separation **342** can include one or more of distillation, membrane filtration (optionally ultrafiltration), chromatographic separation, crystallization, selective precipitation, centrifugation and solvent extraction. These separation techniques can also be applied to additional separations indicated in other methods hereinbelow.

Second Exemplary Method

FIG. **4** is a simplified flow diagram of an exemplary method for realization of value from a first sugar and a second sugar precursor from within a complex mixture of sugars, indicated generally as **400**. Depicted exemplary method **400** includes providing **410** a mixture including a first sugar and at least one second sugar precursor and selectively reacting **420** the first sugar to form a product of the first sugar in product mixture **422**. Depicted exemplary method **400** also includes selectively reacting **430** the second sugar precursor **424** to form the second sugar and separating **440** the product of the first sugar. Optionally, second sugar precursor **424** is separated from product mixture **422** prior to selective reaction **430**. Alternatively or additionally, in some exemplary embodiments of the invention, selectively reacting precursor **430** occurs after separating **440**.

In some exemplary embodiments of the invention, separating **440** includes separating the product of the first sugar and separating the second sugar from product mixture **422**.

In other exemplary embodiments of the invention, separating **440** includes separating the product of the first sugar from the reaction mixture followed by separating the second sugar precursor from the mixture prior to the selectively reacting **430** the precursor to form the second sugar.

In other exemplary embodiments of the invention, separating **440** the product of the first sugar is followed by separating second sugar precursor **424** from product mixture **422**.

In still other exemplary embodiments of the invention, separating **440** includes separating the product of the first sugar from the mixture followed by selectively reacting the precursor of the second sugar to form the second sugar and separating the second sugar from the mixture.

In some exemplary embodiments of the invention, selectively reacting **420** the first sugar includes fermentation. Alternatively or additionally, in some exemplary embodiments of the invention, selectively reacting **430** the precursor includes hydrolysis, optionally acid hydrolysis and/or enzymatic hydrolysis.

Alternatively or additionally, selectively reacting **430** the precursor includes acid catalysis and/or enzymatic catalysis.

Alternatively or additionally, in some exemplary embodiments of the invention, selectively reacting **430** the precursor includes transglucosidation. Optionally, method **400** includes reacting **450** the second sugar to form a second sugar product.

Alternatively or additionally, selective reaction **430** and/or reaction **450** can include oligomerization. Optionally, combination of catalysis with oligomerization produces a similar oligomer chain but with different bonds between the saccharide links. In some exemplary embodiments of the invention, enzymatic catalysis is via fermentation.

Exemplary Mixture Preparation

FIG. **5** is a simplified flow diagram of an exemplary method for preparing a mixture of sugars as described above, indicated generally as **500**. Depicted exemplary method **500** includes providing **510** a lignocellulosic material feed, hydrolyzing **520** the lignocellulosic material feed to form a hydrolyzate **540**. If the hydrolysis is conducted in an acid, method **500** can included de-acidifying **530** the hydrolyzate. Hydrolyzate **540** includes at least one first sugar and at least one second sugar. Optionally, the second sugar is at least partially present as a precursor and hydrolyzing **520** is performed in a counter-current mode. Optionally, at least 5%, optionally at least 10%, optionally at least 15% or intermediate or greater percentages of said lignocellulosic material feed is hemicellulose.

In some exemplary embodiments of the invention, hydrolyzing **520** employs a hydrolysis medium with a wt/wt ratio of mineral acid to (mineral acid+water) of at least 0.35; optionally at least 0.37; optionally at least 0.39; optionally at least 0.41; optionally at least 0.43; optionally at least 0.45 or intermediate or greater ratios. Exemplary mineral acids include, but are not limited to HCl and H_2SO_4.

In other exemplary embodiments of the invention, hydrolyzing **520** employs one or more enzymes to breakdown the lignocellulose provided at **510**. According to various exemplary embodiments of the invention the enzymes can be provided as purified enzymes, cellular extracts, cell supernatants, or a culture containing living cells.

In some exemplary embodiments, hydrolysis **520** employs at least one reactive fluid, to produce soluble sugars from the lignocellulose provided at **510**.

As used in this specification and the accompanying claims the term "reactive fluid" has the meaning ascribed to it in WO 2010/009343; paragraph [0058]. WO 2010/009343 is fully incorporated herein by reference. Alternatively or additionally, one of ordinary skill in the art will be familiar with the contents of WO 2010/009343.

In some exemplary embodiments of the invention, de-acidifying **530** includes selective extraction of HCl with a first extractant comprising a first solvent (S1) characterized by a water solubility of less than 10% and by at least one of: having a delta-P between 5 and 10 $MPa^{1/2}$; and having a delta-H between 5 and 20 $MPa^{1/2}$, whereupon HCl selectively transfers to the first extractant to form an HCl-carrying first extract and an HCl-depleted aqueous feed.

As used herein Delta-P is the polarity related component of Hoy's cohesion parameter and delta-H is the hydrogen bonding related component of Hoy's cohesion parameter.

The cohesion parameter, or, solubility parameter, was defined by Hildebrand as the square root of the cohesive energy density:

$$\delta = \sqrt{\frac{\Delta E_{vap}}{V}}$$

in which ΔEvap and V are the energy or heat of vaporization and molar volume of the liquid, respectively. Hansen extended the original Hildebrand parameter to three-dimensional cohesion parameter. According to this concept, the total solubility parameter delta is separated into three different components, or, partial solubility parameters relating to the specific intermolecular interactions:

$$\delta^2=\delta_d^2+\delta_p^2+\delta_h^2$$

in which delta-D, delta-P and delta-H are the dispersion, polarity, and Hydrogen bonding components, respectively. Hoy proposed a system to estimate total and partial solubility parameters. The unit used for those parameters is $MPa^{1/2}$. A detailed explanation of that parameter and its components could be found in "CRC Handbook of Solubility Parameters and Other Cohesion Parameters", second edition, pages 122-138. That and other references provide tables with the parameters for many compounds. In addition, methods for calculating those parameters are provided.

In some exemplary embodiments of the invention, de-acidifying **530** includes selective extraction of HCl with an alcohol, optionally hexanol and/or 2-ethylhexanol.

Optionally, an amount of at least one of said at least one second sugars, optionally as a precursor, in the product mixture is at least 80; optionally 85; optionally 90%, or intermediate or greater percentages, of a theoretical yield of the same second sugar in the lignocellulosic material feed provided at **510**.

Considering for a moment the concentration of the second sugar and/or its precursor relative to the total amount of sugars present in the mixture, in some cases: if a combined concentration of (the second sugar and its precursor) in the hydrolyzate at **520** is C1 and the combined concentration of (the second sugar and its precursor) in the product mixture **320** after removal of the first sugar product is C2; then C2/C1 is greater than 1.5, optionally greater than 2 and optionally greater than 3. Alternatively or additionally, in some exemplary embodiments of the invention, C2 is at least 30% of saturation concentration at 25° C., optionally at least 50% and optionally at least 70%.

According to various exemplary embodiments of the invention water may be removed at different stages. Optionally, water removal increases a concentration of one or more sugars in the solution. In some exemplary embodiments of the invention, increasing a sugar concentration brings it closer to its saturation point. Optionally, crystallization is more easily accomplished in proximity to the saturation point.

Exemplary Downstream Processing

FIG. **6*a*** is a simplified flow diagram of an exemplary method for preparing a conversion product from a second sugar, indicated generally as **601**.

Depicted exemplary method **601** includes providing **610** a fermentor and fermenting **620** a medium comprising a second sugar (e.g. **232**; **233**; **250**; **424**; or steps **340**; **350**; **540**) the fermentor to produce a conversion product **630**.

FIG. **6*b*** is a simplified flow diagram of an exemplary method for preparing a conversion product from a second sugar and/or a first sugar product indicated generally as **602**.

Depicted exemplary method **602** includes providing an input stream comprising at least one of a second sugar (e.g. **232**; **233**; **250**; **424**; or steps **340**; **350**; **540**) and a product of a first sugar (e.g. **251**; **422**; or step **330**) and converting **621** at least a portion of said input stream to produce a conversion product **631**.

In some exemplary embodiments of the invention, conversion product **631** includes at least one member selected from the group consisting of alcohols, carboxylic acids, amino acids, monomers for the polymer industry and proteins.

Optionally, the method includes processing conversion product **631** to produce a consumer product such as a detergent, a polyethylene-based product, a polypropylene-based product, a polyolefin-based product, a polylactic acid (polylactide)-based product, a polyhydroxyalkanoate-based product and a polyacrylic-based products.

Optionally, the detergent includes a sugar-based surfactant, a fatty acid-based surfactant, a fatty alcohol-based surfactant, or a cell-culture derived enzyme.

Optionally, the polyacrylic-based product is selected from plastics, floor polishes, carpets, paints, coatings, adhesives, dispersions, flocculants, elastomers, acrylic glass, absorbent articles, incontinence pads, sanitary napkins, feminine hygiene products, and diapers.

Optionally, the polyolefin-based products are selected from milk jugs, detergent bottles, margarine tubs, garbage containers, water pipes, absorbent articles, diapers, non wovens, high density polyethylene (HDPE) toys and HDPE detergent packagings.

Optionally, the polypropylene based products are selected from absorbent articles, diapers and non wovens.

Optionally, the polylactic acid based products are selected from packaging of agriculture products and of dairy products, plastic bottles, biodegradable products and disposables.

Optionally, the polyhydroxyalkanoate based products are selected from packaging of agriculture products, plastic bottles, coated papers, molded or extruded articles, feminine hygiene products, tampon applicators, absorbent articles, disposable nonwovens and wipes, medical surgical garments, adhesives, elastomers, films, coatings, aqueous dispersants, fibers, intermediates of pharmaceuticals and binders.

In some exemplary embodiments of the invention, conversion product **631** includes at least one member of the group consisting of ethanol, butanol, isobutanol, a fatty acid, a fatty acid ester, a fatty alcohol and biodiesel.

In some exemplary embodiments of the invention, the method includes processing of conversion product **631** to produce at least one product selected from the group consisting of an isobutene condensation product, jet fuel, gasoline, gasohol, diesel fuel, drop-in fuel, diesel fuel additive, and a precursor thereof.

Optionally, the gasahol is ethanol-enriched gasoline or butanol-enriched gasoline.

Optionally, the product is selected from the group consisting of diesel fuel, gasoline, jet fuel and drop-in fuels. US patent application publication 2009/0035842 describes technology relevant to these applications and is fully incorporated herein by reference.

Some exemplary embodiments of the invention relate to a consumer product, a precursor of a consumer product, or an ingredient of a consumer product produced from a conversion product **631**.

Optionally, the consumer product, precursor of a consumer product, or ingredient of a consumer product includes a conversion product **631** selected from carboxylic and fatty acids, dicarboxylic acids, hydroxylcarboxylic acids, hydroxyl di-carboxylic acids, hydroxyl-fatty acids, methylglyoxal, mono-, di-, or poly-alcohols, alkanes, alkenes, aromatics, aldehydes, ketones, esters, biopolymers, proteins, peptides, amino acids, vitamins, antibiotics, and pharmaceuticals.

Optionally, the product is ethanol-enriched gasoline, jet fuel, or biodiesel.

Optionally, the consumer product, precursor of a consumer product, or ingredient of a consumer product has a ratio of carbon-14 to carbon-12 of about 2.0×10^{-13} or greater.

In some exemplary embodiments of the invention, the consumer product includes an ingredient and an additional ingredient produced from a raw material other than lignocellulosic material. Optionally, the ingredient and said additional ingredient produced from a raw material other than lignocellulosic material are essentially of the same chemical composition.

Optionally, the consumer product includes a marker molecule at a concentration of at least 100 ppb. Marker molecules suitable for use in this context include, but are not limited to, furfural, hydroxy-methyl furfural, products of furfural or hydroxy-methylfurfural condensation, color compounds derived from sugar carmelization, levulinic acid, acetic acid, methanol, galacturonic acid, and glycerol.

In some exemplary embodiments of the invention, conversion product **631** includes xylitol. In some exemplary embodiments of the invention, method **601** and/or **602** includes incorporating the xylitol into an edible product. Edible products include, but are not limited to chewing gum, candy, energy bars, energy gels, energy drinks, cookies and other food products.

In some exemplary embodiments of the invention, conversion product **631** includes rumen bypass protein. In some exemplary embodiments of the invention, method **601** and/or **602** includes incorporating the rumen bypass protein into a livestock feed. Livestock feeds include, but are not limited to hay, straw, silage compressed feed, pelleted feed, oils, mixed rations and crumbled pellets.

Additional Exemplary Method

FIG. **7***a* is a simplified flow diagram of an exemplary method for recovering sugars (optionally monomeric sugars) and/or their products from a complex sugar mixture including oligosaccharides, indicated generally as **700**.

Depicted exemplary method **700** includes selectively reacting **710** a first sugar in a portion of an initial mixture which includes and at least one oligosaccharide to form a product mixture **720** comprising a product **721** of the first sugar. Optionally, the initial mixture includes one or more monomeric sugars. Depicted exemplary method **700** also includes producing **730** an oligomer rich sugar fraction with a ratio of at least one of said at least one oligosaccharide to a total sugar concentration greater than a ratio of the same components in product mixture **720**. Optionally, method **700** includes hydrolyzing **740** the oligomer rich sugar fraction to produce additional monomeric sugars **750**. Exemplary ways to perform hydrolysis **740** are described in provisional patent application U.S. 61/524,839 which is fully incorporated herein by reference.

Depicted exemplary method **700** includes separating **760** product **721** of the first sugar from product mixture **720**.

Optionally, method **700** includes separating **770** at least one of the at least one additional monomeric sugars from product mixture **720**. In some exemplary embodiments of the invention, separation **770** includes crystallization. Optionally, xylose is crystallized during separation **770**.

In some exemplary embodiments of the invention, selectively reacting **710** the first monomeric sugar yields an alcohol **790** as a reaction product. Optionally, the first monomeric sugar is glucose and the alcohol includes ethanol.

In the depicted exemplary embodiment, method **700** includes use of alcohol **790** to aid in crystallization **795** of at least one of said at least one additional monomeric sugars. In some exemplary embodiments of the invention, the monomeric sugar to be crystallized is xylose. In some exemplary embodiments of the invention, separation **770** includes removal of water to increases a concentration of each sugar in the mixture. Alternatively or additionally, separation **770** includes addition of alcohol **790** at a higher concentration than that which was present in the mixture prior to separation **760** by distillation **797**. Optionally, separation **770** by crystallization employs alcohol **790** at a concentration of 15; 20; 25; 30; 35; 40; 45; 50; 55; 60; 65; 70; 75; 80; 85; 90% or intermediate concentrations (W/W).

In some exemplary embodiments of the invention, alcohol **790** is distilled **797** from product mixture **720** as a means of separation **760** of product **721** and re-introduced during crystallization **795** at a desired concentration. Optionally, these embodiments include a repetition of separation **760** (indicated by double headed arrow) to recover alcohol **790**. These embodiments are advantageous in that they can achieve a high alcohol concentration which makes it feasible to crystallize sugars that are relatively far from their saturation point. However, there is an energy cost to re-distilling the alcohol for recovery.

In other exemplary embodiments of the invention (not depicted), separation **770** by crystallizing **795** at least one of the at least one additional monomeric sugars is followed by distilling **797** of alcohol **790** from the product mixture. These embodiments are advantageous in that they involve only a single distillation, but cannot achieve the high alcohol concentrations during crystallization which are possible if distillation is conducted prior to crystallization unless alcohol is introduced from an outside source, or from a previous round of purification.

In some exemplary embodiments of the invention, producing **730** an oligomer rich sugar fraction includes crystallization **795** of at least one of said at least one oligosaccharide from product mixture **720**. Optionally, this crystallization employs an alcohol **790** produced by selectively reacting **710**. Alcohol **790** can be used to aid in crystallization of an oligosaccharide as described above for monomeric sugars.

According to various exemplary embodiments of the invention separation **770** produces either crystals of oligosaccharide, or a liquid mixture enriched in oligosaccharides. In either case, these oligomeric sugars can be used to produce **730** the oligomer rich sugar fraction which can subsequently be hydrolyzed **740** to produce additional monomeric sugars.

FIG. **7***b* is a simplified flow diagram of another exemplary method for recovering sugars (optionally monomeric sugars) and/or their products from a complex sugar mixture including oligosaccharides, indicated generally as **701**.

Depicted Exemplary method **701** includes selectively reacting **710** a first sugar in an initial mixture which includes a first sugar and at least one oligosaccharide **722** to form a product mixture **720** comprising a product **721** of the first sugar. Depicted method **701** also includes separating **761** product **721** from product mixture **720** and hydrolyzing **741** oligosaccharide **722** to produce additional first sugar **751**.

Optionally, the initial mixture includes a second sugar. In some exemplary embodiments of the invention, the method includes separating the second sugar.

Another Additional Exemplary Method

FIG. **8***a* is a simplified flow diagram of an exemplary method for recovering ethanol and a crystallized non-glucose sugar from a complex sugar mixture including oligosaccharides, indicated generally as **801**.

Depicted exemplary method **801** includes fermenting **810** glucose in a portion of an initial mixture which includes at least one additional monomeric sugar and at least one oligosaccharide to form a product mixture **812** including ethanol and using **820** the ethanol to aid in crystallization of at least one non-glucose sugar in the product mixture to produce crystals **821**. Optionally, the non-glucose sugar is xylose.

FIG. **8***b* is a simplified flow diagram of an exemplary method according to FIG. **8***a* in which crystals **821** are monomeric sugar crystals indicated generally as method **802**.

Depicted exemplary method **802** begins with separation **830** of at least one non-glucose sugar as crystals **821***a* comprising primarily at least one of the at least one additional monomeric sugar and an oligosaccharide enriched mother liquor **822***a*.

Optionally, method **802** includes hydrolyzing **840** oligosaccharide enriched mother liquor **822***a* to produce additional monomeric sugars **841***a*.

FIG. **8***c* is a simplified flow diagram of an exemplary method according to FIG. **8***a* in which crystals **821** are oligosaccharide crystals indicated generally as method **804**.

Depicted exemplary method **804** begins with separation **830** of crystals **821***b* comprising primarily one or more oligosaccharides and a monomeric sugar enriched mother liquor **822***b*.

In the depicted embodiment, method **804** includes crystallizing **850** at least one monomeric sugar from monomeric sugar enriched mother liquor **822***b*. Optionally, an alcohol, such as ethanol **860** is used to aid in crystallization **850**.

In some exemplary embodiments of the invention, crystals **821***b* are hydrolyzed **824** to produce additional monomeric sugars **841***b*. In some exemplary embodiments of the invention, these additional monomeric sugars include glucose.

Exemplary System

FIG. **9** is schematic diagram of an exemplary system for processing a sugar mixture indicated generally system **900**. Depicted exemplary system **900** includes a fermentor **910** adapted to deliver a stream of spent media **912** to a separation unit **920** adapted to separate solids **922** from spent media **912** and deliver a supernatant stream **924**. According to various exemplary embodiments of the invention separation unit **920** includes centrifugation components and/or filtration components.

Depicted exemplary system **900** also includes a distillation unit **930** adapted to distill an alcohol **932** from supernatant stream **924** to produce a modified supernatant **934**. Adaptation to distill an alcohol can include implementation of one or more design changes which take into account the alcohol to be distilled and/or the composition of supernatant stream **924**. For example, if the alcohol to be distilled has a high boiling point, a stronger heat source may be provided. Alternatively or additionally, if there are components in stream **924** with a boiling pint close to that of the alcohol in question, a long distillation column, or two or more distillation columns in series, may be incorporated into distillation unit **930** to improve separation of the alcohol from other components. In some exemplary embodiments of the invention, the alcohol is ethanol which can be recovered at up to 95% purity.

Depicted exemplary system **900** also includes a primary crystallization module **940** adapted to receive at least a portion of modified supernatant **934** from distillation unit **930** and crystallize at least one sugar (crystals **942**) therefrom to produce a mother liquor **944**. Optionally, distillation unit **930** also delivers at least a portion of alcohol **932** to crystallization module **940**. Alternatively or additionally, crystallization module **940** receives alcohol from an independently provided alcohol reservoir (not depicted). Optionally, separation of alcohol **932** from stream **934** followed by re-mixing of these components contributes to an ability to increase the alcohol concentration in stream **934**. In some exemplary embodiments of the invention, increasing the alcohol concentration improves one or more crystallization parameters. Crystallization parameters include, but are not limited to, yield and purity of crystals. Alcohol concentrations during crystallization are optionally as described above in the context of FIG. **7***a*.

In some exemplary embodiments of the invention, fermentor **910** converts glucose to ethanol which is distilled by distillation unit **930** so that modified supernatant **934** is substantially free of glucose. According to these exemplary embodiments of the invention crystals **942** are of a non-glucose sugar. According to various exemplary embodiments of the invention this sugar can be monomeric or oligomeric (e.g. disaccharide or higher).

Optionally, system **900** includes a secondary crystallization module **950** adapted to receive at least a portion of alcohol **932** from distillation unit **930** and crystallize at least one additional sugar (crystals **952**) from mother liquor **944** to produce a spent mother liquor **954**. Optionally, alcohol aids in crystallization as described above in the context of module **940**. Alternatively or additionally, secondary crystallization module **950** receives alcohol from an independently provided alcohol reservoir (not depicted).

Depicted exemplary system **900** also includes an alcohol recovery module **960** adapted to distill alcohol **962** from mother liquor **944** and/or spent mother liquor **954**. Module **960** also produces a liquor residue **964**. In some exemplary embodiments of the invention, residue **964** is subject to anaerobic fermentation in an anaerobic fermentation module (not depicted). Optionally, this anaerobic fermentation produces a usable energy source such as methane. In some exemplary embodiments of the invention, methane produced in this manner is used to provide heat energy for various system components (e.g. distillation module **930** and/or alcohol recovery module **960**).

In some exemplary embodiments of the invention, exemplary system **900** also includes a hydrolysis module **970**. Hydrolysis module **970** produces additional monomeric sugars **972** from an input material including dimeric sugars and other soluble oligomeric sugars. According to various exemplary embodiments of the invention the input material includes one or more of crystals **942** produced by primary crystallization module **940**; mother liquor **944**; crystals **952** produced by secondary crystallization module **950** and spent mother liquor **954**. Optionally, additional monomeric sugars **972** are delivered to fermentor **910** (as depicted) and/or to crystallization module **940** and/or **950** (not shown) by a recycling pump (not depicted).

According to various exemplary embodiments of the invention system **900** includes one or more pumps (not depicted) to control flows among and between components of the system.

Depicted exemplary system **900** includes a controller **990** adapted to control at least one of the at least one pumps. Optionally, system **900** includes one or more detectors (not shown) configured to provide data pertaining to at least one system parameter to controller **990**. In some exemplary embodiments of the invention, controller **990** is responsive to the data. System parameters include, but are not limited to, concentration of specific sugars at specific points, total sugar concentration at specific points, alcohol concentration, temperatures, flow rates and acid concentration.

Additional Exemplary Method

FIG. **10** is a simplified flow diagram of an exemplary method according to some embodiments of the invention depicted generally as **1000**. Depicted exemplary method **1000** produces a first sugar product **1011** and a product of a second sugar from a mixture **1010** of sugars. Optionally, the product of the second sugar is xylitol.

According to depicted exemplary method **1000**, separation of 1st sugar product **1011** from mixture **1010** produces a modified mixture **1020**. In some exemplary embodiments of the invention, mixture **1010** is provided as an aqueous solution of sugars. In some exemplary embodiments of the invention, mixture **1020** is at least 35, optionally at least 40, optionally 45, optionally 50% or intermediate or greater percentages of xylose on a weight basis relative to total sugars. In the depicted exemplary embodiment, ultrafiltration **1022** of modified mixture **1020** produces a concentrated mixture **1024**. In some exemplary embodiments of the invention, mixture **1024** includes 45, optionally 50, optionally 55, optionally 60% or intermediate or greater percentages of total sugars on a weight basis.

In the depicted exemplary embodiment, concentrated mixture **1024** is subject to chromatographic separation **1030**. Chromatographic separation enriches the mixture for xylose, but may also dilute the mixture. In the depicted exemplary embodiment, xylose fraction **1040** includes 65, optionally 70, optionally 80, optionally 85% or intermediate or greater percentages of xylose on a weight basis relative to total sugars in the solution. Alternatively or additionally, fraction **1040** may include 2, optionally 3, optionally 4% or intermediate or greater percentages of mannose on a weight basis relative to total sugars in the solution. Alternatively or additionally, fraction **1040** may include 4, optionally 5, optionally 6% or intermediate or greater percentages of galactose on a weight basis relative to total sugars in the solution. Alternatively or additionally, fraction **1040** may include 1, optionally 2, optionally 3% or intermediate or greater percentages of arabinose on a weight basis relative to total sugars in the solution.

In the depicted exemplary embodiment, concentration **1050** increases the total sugar concentration to 65, optionally 70, optionally 75, optionally 80% or intermediate or greater percentages. Concentration **1050** brings xylose closer to its saturation point.

Crystallization **1060** produces crystals **1062** of a second sugar (e.g. xylose) and a mother liquor **1070**. Optionally, an organic solvent, such an alcohol (e.g. ethanol or methanol) is added to the solution during crystallization **1060** to aid in precipitation of sugar crystals. Exemplary alcohol concentrations are provided above in the context of FIG. **7***a*.

Crystals **1062**, which are substantially pure, can be subjected to hydrogenation **1124** to produce a corresponding alcohol. For example, if crystals **1062** are xylose crystals, hydrogenation will produce xylitol. Since hydrogenation is not typically a selective reaction, crystallization **1060** contributes to an ability to produce a desired sugar-alcohol at relatively high purity.

Returning now to crystallization **1060**, the resultant mother liquor **1070** can be subject to additional chromatographic separation together with an additional amount of concentrated mixture **1024**. Optionally, this allows at least a portion of xylose in mother liquor **1070** to be recovered by an additional round of crystallization **1060**. Optionally, remaining sugars **1042** can be sent to anaerobic fermentation **1044** to produce an energy source, such as methane.

Exemplary Sugar Compositions

Some exemplary embodiments of the invention relate to sugar compositions which exist as production intermediates in various methods described herein.

For example, practice of the procedure outlined in FIG. **10** might produce, as an intermediate product, a sugar composition including at least 25; optionally 30; optionally 35% xylose by weight relative to total sugar concentration with a detectable amount of at least one alpha-bonded di-glucose and a detectable amount of at least one beta-bonded di-glucose. Optionally, the alpha-bonded di-glucose includes maltose and/or isomaltose and/or trehalose. Optionally, the beta-bonded di-glucose includes gentiobiose and/or sophorose and/or cellobiose. Compositions of this general type might occur at, for example, **1020** in FIG. **10**. According to various exemplary embodiments of the invention the alpha bonded di-glucose is optionally present at a level of at least 10, optionally at least 50, optionally at least 100, optionally at least 500, optionally at least 1000 PPM or intermediate or greater levels. Alternatively or additionally, according to various exemplary embodiments of the invention the beta bonded di-glucose is optionally present at a level of at least 10, optionally at least 50, optionally at least 100, optionally at least 500, optionally at least 1000 PPM or intermediate or greater levels.

Optionally, the composition includes at least 40; optionally at least 42; optionally at least 45; optionally at least 47; optionally at least 50% total sugars. Compositions of this general type might occur at, for example, **1024** in FIG. **10**.

Optionally, the composition is provided as a solution, for example an aqueous solution.

In some exemplary embodiments of the invention, the composition includes less than 90; optionally 80; optionally 70% xylose of total sugars on a weight basis.

Alternatively or additionally, in some exemplary embodiments of the invention the composition includes glucose at a concentration of at least 0.001; optionally at least 0.01; optionally at least 0.1% of total sugars on a weight basis. Alternatively or additionally, in some exemplary embodiments of the invention the composition includes glucose at a concentration of less than 5; optionally 3; optionally 1% of total sugars on a weight basis.

Alternatively or additionally, in some exemplary embodiments of the invention the composition includes at least 0.001; optionally 0.01; optionally 0.1% arabinose of total sugars on a weight basis.

Alternatively or additionally, in some exemplary embodiments of the invention the composition includes at least 0.001; optionally 0.0005; optionally 0.0001% non-volatile fermentation product on a weight basis. As used in this specification and the accompanying claims the term "non volatile fermentation products" includes but is not limited to: lactic acid, succinic acid, fatty acids, esters of fatty acids and proteins.

Alternatively or additionally, practice of the procedure outlined in FIG. **10** might produce, as an intermediate product, a sugar solution comprising (by weight relative to total sugar concentration) at least 60% xylose, at least 100 PPB of a marker molecule and 0.001% to 10% oligosaccharides. Optionally, the oligosaccharides include maltose and/or isomaltose and/or trehalose. Optionally, the oligosaccharides include gentiobiose, sophorose and cellobiose.

According to various exemplary embodiments of the invention the marker molecule includes at least one, optionally at least two, optionally at least three of furfural, hydroxy-methyl furfural, products of furfural or hydroxymethylfurfural condensation, color compounds formed on heating a sugar, levulinic acid, acetic acid, methanol, galacturonic acid, an alcohol of more than four carbon atoms, betaine, amino acids, proteins phosphate and glycerol.

Alternatively or additionally, the composition includes at least one; optionally at least two; optionally at least three fermentation residue(s). According to various exemplary embodiments of the invention the fermentation residue includes a component of an ingredient selected from the group consisting of sugar molasses, yeast extract and corn steep liquor. Optionally, fermentation residues can serve as marker molecules. Thus, there are marker molecules indicative of hydrolysis of a lignocellulosic substrate, and additional marker molecules indicative of fermentation of sugars in the resultant hydrolyzate.

Optionally, the composition includes glucose at a concentration of 0.001; optionally 0.01; optionally 0.1% of total sugars on a weight basis. Alternatively or additionally, the composition optionally includes glucose at a concentration of not more than 5; optionally 3; optionally 1% of total sugars on a weight basis.

Alternatively or additionally, the composition optionally includes arabinose at a concentration of at least 0.001; optionally 0.01; optionally 0.1% of total sugars on a weight basis.

Alternatively or additionally, the composition optionally includes 0.001% non-volatile fermentation product on a weight basis.

In some exemplary embodiments of the invention, the concentration of marker molecule does not exceed 0.5%. Optionally, a total concentration of the two, optionally the three, marker molecules does not exceed 0.5%.

Optionally, the composition includes at least 60% total sugars.

Optionally, the composition includes mannose and/or galactose and/or arabinose.

In some exemplary embodiments of the invention, the solution includes at least 3% mannose relative to total monosaccharides by weight.

Alternatively or additionally, the composition includes at least 5% galactose relative to total monosaccharides by weight.

Alternatively or additionally, the composition includes at least 2% arabinose relative to total monosaccharides by weight.

Compositions of this general type might occur at, for example, **1040** or **1050** in FIG. **10**.

Additional Exemplary Composition

Some exemplary embodiments of the invention relate to sugar compositions which remain after glucose and xylose have been removed from an initial mixture **1010**. These embodiments correspond, for example, to mother liquor **1070** in FIG. **10**. This type of sugar composition includes at least one of:

alpha-bonded di-glucose;

beta-bonded di-glucose; and

arabinose;

together with 0.01%-20% xylose by weight relative to total sugar concentration and at least 100 PPB of a marker molecule.

Optionally, the composition is provided as a solution, for example an aqueous solution.

In some exemplary embodiments of the invention, the composition includes glucose at a concentration of at least 0.001% but not more than and 5%; optionally 3; optionally 1% of total sugars on a weight basis.

In some exemplary embodiments of the invention, the composition includes at least 0.001% non-volatile fermentation product on a weight basis.

In some exemplary embodiments of the invention, the alpha-bonded di-glucose includes at least one member of the group consisting of maltose, isomaltose and trehalose. Alternatively or additionally, in some exemplary embodiments of the invention, the beta-bonded di-glucose includes at least one member selected from the group consisting of gentiobiose, sophorose and cellobiose.

In some exemplary embodiments of the invention, the composition includes at least 40% total sugars.

Optionally, the marker molecule is selected from the group consisting of furfural, hydroxy-methyl furfural, products of furfural or hydroxy-methylfurfural condensation, color compounds formed on heating a sugar, levulinic acid, acetic acid, methanol, galacturonic acid, an alcohol of more than four carbon atoms, betaine, amino acids, proteins phosphate and glycerol. Optionally, the composition includes at least two, optionally at least three, marker molecules.

Alternatively or additionally, the composition includes at least one fermentation residue. Optionally, the fermentation residue includes a component of an ingredient selected from the group consisting of sugar molasses, yeast extract and corn steep liquor.

In some exemplary embodiments of the invention, the concentration of marker molecule does not exceed 0.5%. Optionally, a total concentration of the two, optionally the three, marker molecules does not exceed 0.5%.

Optionally, the composition includes mannose and/or galactose and/or arabinose.

In some exemplary embodiments of the invention, the solution includes at least 3% mannose relative to total monosaccharides by weight.

Alternatively or additionally, the composition includes at least 5% galactose relative to total monosaccharides by weight.

Alternatively or additionally, the composition includes at least 2% arabinose relative to total monosaccharides by weight.

Exemplary Logic Hierarchy

FIG. **11** is a logic hierarchy illustrating approaches to separating products of value from lignocelluloses according to various exemplary embodiments of the invention indicated generally as **1100**.

Exemplary embodiments depicted by method **1100** feature a one stage hydrolysis **1130** as described hereinabove in the context of FIG. **1**. Such a hydrolysis produces a sugar mixture **1132**. Without considering the quantitative yield of any specific sugars in mixture **1132**, logic hierarchy **1100** includes various strategies for exploiting two or more sugar components in the mixture.

The depicted exemplary embodiments of the invention implement a selective conversion **1140** of one sugar to produce a conversion product **1142**. In some exemplary embodiments of the invention, conversion **1140** includes a fermentation reaction. Optionally, conversion **1140** includes a chemical reaction and/or an enzymatic reaction not mediated by a microorganism. In some exemplary embodiments of the invention, conversion **1140** includes fermentation of glucoses and conversion product **1142** includes ethanol.

A simplified sugar mixture **1150** remains following separation of conversion product **1142**. According to various exemplary embodiments of the invention it is possible to perform a selective conversion **1180** of a second sugar to form an additional product and/or to crystallize **1170** one or more second sugar(s). In one exemplary embodiment of the invention, xylose serves as a second sugar in simplified sugar mixture **1150**. According to this embodiment, xylose can be crystallized **1170** and then selectively converted **1180** by hydrogenation to xylitol.

Regardless of the first sugar and second sugar employed, selective conversion **1140** followed by removal of conversion product **1142** contributes to an ability to selectively convert **1180** the second sugar by providing a simplified sugar mixture **1150**.

In some exemplary embodiments of the invention, crystallization **1170** is performed to remove an interfering sugar from mixture **1150** and permit selective conversion **1180** of a desired second sugar to form a desired product.

It is expected that during the life of this patent many chromatographic separation techniques will be developed and the scope of the invention is intended to include all such new technologies a priori.

As used herein the term "about" refers to ±10%; optionally ±5%; optionally ±1%, optionally ±0.1%.

Although the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art. Accordingly, it is intended to embrace all such alternatives, modifications and variations that fall within the spirit and broad scope of the appended claims.

Specifically, a variety of numerical indicators have been utilized. It should be understood that these numerical indicators could vary even further based upon a variety of engineering principles, materials, intended use and designs incorporated into the invention. Additionally, components and/or actions ascribed to exemplary embodiments of the invention and depicted as a single unit may be divided into subunits. Conversely, components and/or actions ascribed to exemplary embodiments of the invention and depicted as sub-units/individual actions may be combined into a single unit/action with the described/depicted function.

Alternatively, or additionally, features used to describe a method can be used to characterize an apparatus and features used to describe an apparatus can be used to characterize a method.

It should be further understood that the individual features described hereinabove can be combined in all possible combinations and sub-combinations to produce additional embodiments of the invention. The examples given above are exemplary in nature and are not intended to limit the scope of the invention which is defined solely by the following claims. Specifically, the invention has been described in the context of sugar mixtures resulting from acid hydrolysis of a lignocellulosic substrate but might also be used in the context of sugar mixtures formed by other processes.

All publications, patents and patent applications mentioned in this specification are herein incorporated in their entirety by reference into the specification, to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated herein by reference. In addition, citation or identification of any reference in this application shall not be construed as an admission that such reference is available as prior art to the present invention.

The terms "include", and "have" and their conjugates as used herein mean "including but not necessarily limited to".

Additional objects, advantages, and novel features of various embodiments of the invention will become apparent to one ordinarily skilled in the art upon examination of the following example, which is not intended to be limiting. Additionally, various embodiments and aspects of the present invention as delineated hereinabove and as claimed in the claims section below finds experimental support in the following examples.

EXAMPLE

Reference is now made to the following example, which together with the above descriptions, illustrates some embodiments of the invention in a non limiting fashion.

Example

Projected Compositions of Sugar Mixtures after Removal of Glucose by Fermentation and Distillation of Ethanol

This example projects expected relative concentrations of monosaccharides in de-acidified hydrolyzates described in PCT IL 2011/000509, which is fully incorporated herein by reference, following removal of substantially all glucose by fermentation and distillation. This example also presumes that the fermentation reaction is specific and that other monosaccharides are not fermented to any significant degree.

In order to prepare the initial sugar mixtures, which would serve as the fermentation substrate, various lignocellulosic materials were introduced into a six stage hydrolysis reactor series in a counter-current operation as described in U.S. provisional application 61/483,777 filed May 9, 2011 and entitled "Hydrolysis systems and methods". This application is fully incorporated herein by reference.

Briefly, an aqueous solution of 42% HCl was introduced continually at a temperature of 10-15° C. for 24 hours. The hydrolyzate was collected, HCl was removed by extraction and the de-acidified hydrolyzate was concentrated to give a sugar composition. Analysis of actual results of monosaccharides are summarized in Table 1 (before). Disaccharide data is not presented but may be found in PCT IL 2011/000509. These actual results are calculated as % from sample's refractive total saccharides (%/RTS).

Table 1 also includes a calculated projection of relative sugar concentrations (as a % of total monosaccharides) following removal of glucose by fermentation/distillation (after).

The assayed substrates included two samples of pine wood, sugar cane bagasse and eucalyptus wood.

Results presented in Table 1 indicate that selective fermentation of glucose (optionally followed by removal of the resultant ethanol from the hydrolyzate mixture) increases the relative proportion of xylose. In the case of pine wood, xylose is the major monosaccharide component after glucose is eliminated.

Although di-saccharides and higher oligosaccharides account for a significant proportion of total sugars in the mixture, they are divided among a large number of different molecules. Alternatively or additionally, di-saccharides and higher oligosaccharides can be separated from a mixture of monosaccharides using chromatographic techniques. For this reason it seems that selective precipitation of xylose from glucose depleted mixtures will be feasible. It is envisioned that selective precipitation can be aided by cooling and/or addition of a non-aqueous solvent, such as ethanol. Optionally, ethanol produced by glucose fermentation can be used for this purpose.

TABLE 1

Monosaccharides in hydrolyzates of various substrates before and after selective removal of glucose

substrate	status	other	Arabinose	Galactose	Glucose	Xylose	Mannose	Sum
Pine 1	before	0.1 (Rhamnose)	1.6	2.7	27.7	7.0	7.4	46.5
	after	0.5	8.5	14.3	NA	37.2	39.3	NA
Pine 2	before	NA*	0.3	0.8	36.0	8.0	1.0	46
	after	NA*	3.0	7.9	NA	79.2	9.9	NA
Bagasse	before	2.4 (fructose)	2.2	7.2	48.7	4.9	4.8	70.2
	after	11.2	10.2	33.5	NA	22.8	22.3	NA
Eucalyptus	before	3.38 (fructose)	2.6	7.24	46.1	8.27	5.83	73.42
	after	12.4	9.5	26.5	NA	30.3	5.83	21.33

*NA indicates not applicable

In those cases where crystallization of xylose proves difficult due to the presence of another sugar in a large amount (e.g. bagasse or eucalyptus where a large amount of galactoses is present) the interfering sugar can be removed prior to such crystallization if necessary. For example galactose has a solubility of 683 g/L (Wikipedia) in water while xylose has a solubility of 1250 g/L in water (Merck index). This suggests that galactose could be removed prior to xylose via selective crystallization of galactose.

The invention claimed is:

1. A lignocellulosic hydrolysate comprising:

(a) at least 60% xylose by weight relative to total sugar concentration;

(b) a total concentration of 0.00001% to 0.5% by weight relative to total sugar concentration of at least two marker molecules, wherein said marker molecules are selected from furfural, hydroxy-methylfurfural, and acetic acid;

(c) 0.001% to 10% oligosaccharides by weight relative to total sugar concentration; and

(d) at least 3% mannose by weight relative to total monosaccharides.

2. The lignocellulosic hydrolysate according to claim **1**, comprising at least three marker molecules.

3. The lignocellulosic hydrolysate according to claim **1**, comprising between 0.001% and 5% glucose of total sugars on a weight basis.

4. The lignocellulosic hydrolysate according to claim **1**, comprising at least 0.001% arabinose of total sugars on a weight basis.

5. The lignocellulosic hydrolysate according to claim **1**, wherein said oligosaccharides include at least one member selected from the group consisting of maltose, isomaltose and trehalose.

6. The lignocellulosic hydrolysate according to claim **1**, wherein said oligosaccharides include at least one member selected from the group consisting of gentiobiose, sophorose and cellobiose.

7. The lignocellulosic hydrolysate according to claim **1**, comprising at least one sugar selected from the group consisting of galactose and arabinose.

8. The lignocellulosic hydrolysate according to claim **1**, comprising at least 5% galactose relative to total monosaccharides by weight.

9. The lignocellulosic hydrolysate according to claim **1**, comprising at least 2% arabinose relative to total monosaccharides by weight.

10. The lignocellulosic hydrolysate according to claim **1**, **3**, or **9**, wherein said marker molecules comprise furfural and hydroxy-methylfurfural.

11. The lignocellulosic hydrolysate according to claim **1**, **3**, **8**, or **9**, further comprising at least 100 PPB 2-ethylhexanol.

12. The lignocellulosic hydrolysate according to claim **1**, comprising less than 90% of said xylose by weight relative to total sugar concentration.

13. The lignocellulosic hydrolysate according to claim **1**, wherein said lignocellulosic hydrolysate is provided as an aqueous solution.

14. The lignocellulosic hydrolysate according to claim **13**, wherein said lignocellulosic hydrolysate comprises at least 40% total sugars by weight.

15. The lignocellulosic hydrolysate according to claim **1**, wherein said lignocellulosic hydrolysate has not been purified by crystallization.

16. The lignocellulosic hydrolysate according to claim **1**, comprising at least 0.01% of said oligosaccharides by weight relative to total sugar concentration.

17. The lignocellulosic hydrolysate according to claim **1**, comprising at least 0.1% of said oligosaccharides by weight relative to total sugar concentration.

18. The lignocellulosic hydrolysate according to claim **1** or **3**, further comprising at least 100 PPB hexanol.

19. The lignocellulosic hydrolysate according to claim **1**, wherein said marker molecules comprise acetic acid.

20. The lignocellulosic hydrolysate according to claim **1**, further comprising levulinic acid or methanol.

21. A lignocellulosic hydrolysate comprising:

(a) at least 60% xylose by weight relative to total sugar concentration;

(b) a total concentration of 0.00001% to 0.5% by weight relative to total sugar concentration of at least three marker molecules, wherein said marker molecules are furfural, hydroxy-methylfurfural, and acetic acid;

(c) 0.001% to 10% oligosaccharides by weight relative to total sugar concentration;

(d) at least 2% arabinose by weight relative to total monosaccharides;

(e) at least 3% mannose by weight relative to total monosaccharides; and

(f) at least 100 PPB 2-ethylhexanol.

22. A lignocellulosic hydrolysate comprising:

(a) at least 60% xylose by weight relative to total sugar concentration;

(b) a total concentration of 0.00001% to 0.5% by weight relative to total sugar concentration of at least two marker molecules, wherein said marker molecules are selected from furfural, hydroxy-methylfurfural, and acetic acid;

(c) 0.001% to 10% oligosaccharides by weight relative to total sugar concentration; and

(d) at least 5% galactose by weight relative to total monosaccharides.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 10,240,217 B2
APPLICATION NO. : 14/033205
DATED : March 26, 2019
INVENTOR(S) : Robert Jansen et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

On the Title Page

Item (30), insert --Aug. 1, 2011 (WO)........PCT/US2011/046153--.

Signed and Sealed this
Eighteenth Day of June, 2019

Andrei Iancu
Director of the United States Patent and Trademark Office